

(19)



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European Patent Office
Office européen des brevets



(11)

EP 0 894 620 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
03.02.1999 Bulletin 1999/05

(51) Int. Cl.⁶: B32B 27/18, C08G 63/66,
C08G 63/688, C08L 67/02,
C08L 101/00, G02B 5/22,
F21V 9/04, C08K 5/45,
C08K 5/29

(21) Application number: 97917429.9

(86) International application number:
PCT/JP97/01341

(22) Date of filing: 16.04.1997

(87) International publication number:
WO 97/38855 (23.10.1997 Gazette 1997/45)

YAO

(84) Designated Contracting States:
DE FR GB NL

• KOIKE, Masahiro
12-21-204, Tomobuchi-cho 2-chome
Osaka 534-0016 (JP)
• SUZUKI, Yasuko
Osaka 573-0076 (JP)
• SAKURAI, Kazuo
Hyogo 670-0033 (JP)
• INDO, Takashi
6-2-401, Tomobuchi-cho 1-chome
Osaka 534-0016 (JP)
• IGARASHI, Kouei
6-4-101, Tomobuchi-cho 1 chome
Osaka 534-0016 (JP)

(30) Priority: 18.04.1996 JP 122705/96
09.09.1996 JP 261354/96
09.09.1996 JP 261355/96
09.09.1996 JP 261356/96
06.02.1997 JP 39788/97

(74) Representative:
Henkel, Feiler, Hänel
Möhlstrasse 37
81675 München (DE)

(71) Applicant: KANEBO LTD.
Sumida-ku, Tokyo 131 (JP)

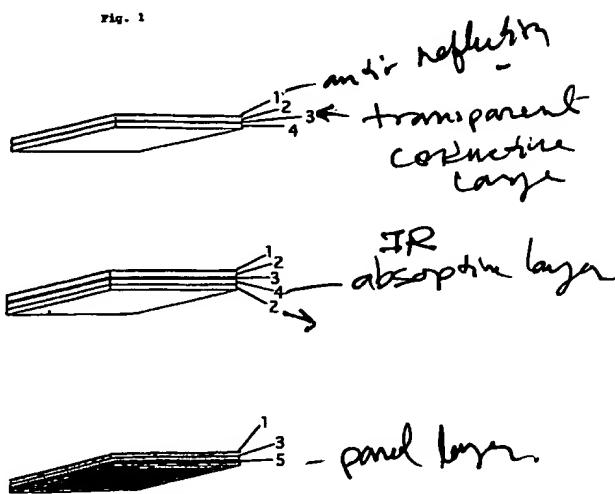
(72) Inventors:
• YAO, Kenji
6-7-305, Tomobuchi-cho 1 chome
Osaka 534-0016 (JP)

(54) NEAR INFRARED RAY ABSORPTION FILM AND MULTI-LAYERED PANEL INCLUDING SAME

(57) Disclosed is a film or panel having excellent near-infrared absorbability or, that is, excellent near-infrared shieldability, and having a high degree of visible ray transmittance and good color tone.

To produce the near-infrared-absorbing film or panel having good color tone while the near-infrared-absorbing dye to be therein is kept stable, the dye and the binder resin for the dye are specifically selected, and the production method is also specifically selected. In addition, for the purpose of producing the film or panel while the dye to be therein is kept stable and for the purpose of making the film or panel have additional functions such as electromagnetic radiation absorbability, the film or panel is made to have a multi-layered structure.

Fig. 1



Description**TECHNICAL FIELD**

5 [0001] The present invention relates to an infrared absorbing film, which absorbs near-infrared rays as emitted by image output devices such as plasma displays, lighting appliances or the like so as to cut off the penetration of the rays through the film, thereby preventing remote-control infrared communication ports that employ the rays falling within an infrared range for communication from malfunctioning and even preventing the appliances to be controlled by those remote-control devices from malfunctioning. More precisely, the invention relates to a multi-layered film or a panel of a
 10 multi-layered sheet that comprises an absorbing layer having a near-infrared absorbing effect and an electromagnetic radiation shielding effect as combined with a transparent conductor. It further relates to a near-infrared cut-off filter to be used, for example, for light-receiving sensitivity correction or color tone correction in photodiodes or solid image sensor (CCD) cameras as used in light-receiving devices or image pickup devices in optical appliances, and also to a film or panel to be used for detecting forged cash cards and ID cards. The multi-layered sheet as referred to herein is one
 15 as prepared by laminating functional films, which include the film of the invention, on a substrate having a shape-retaining function, generally on a transparent substrate.

BACKGROUND ART

20 [0002] As near-infrared-absorbing panels, known are glass filters having a metal deposit film formed thereon, and metal ion-containing phosphate glass filters. However, as being based on the phenomenon of interference, the former are problematic in that they are negatively influenced by reflected light and that their infrared-absorbing capabilities do not often correspond to luminous quantities. In addition, their production costs are high. On the other hand, the latter are also problematic in that they absorb moisture and that they are produced in a complicated process. Moreover, the
 25 conventional glass filters are further problematic in that they are heavy and are easily cracked, and, in addition, they are difficult to work.

[0003] In order to solve these problems, various plastic materials having absorption characteristics in the infrared range have been proposed for producing plastic filters. For example, as in Japanese Patent Application Laid-Open (JP-A) Hei-6-214113, known are panels which are produced by dissolving a metal phthalocyanine compound in a monomer of methyl methacrylate followed by polymerizing the monomer. Also known are near-infrared-absorbing panels which are produced by kneading a phthalocyanine compound or an anthraquinone or cyanine compound in a resin melt followed by sheeting the resulting mixture through extrusion.

[0004] However, the panel production comprises high-temperature melt extrusion and polymerization, and therefore could not apply to near-infrared-absorbing materials which are thermally unstable or to those which are decomposed or deteriorated through chemical reaction under the process condition. Accordingly, the near-infrared-absorbing characteristics of the panels produced are not satisfactory. In addition, when panels are used in displays, etc., not only their near-infrared-absorbing characteristics but also their color tone characteristics are important. To control the color tone of panels, in general, a plurality of different dyes must be mixed. However, when mixed with other dyes, some dyes having near-infrared-absorbing characteristics may change their characteristics, or may even change their near-infrared-absorbing capabilities through chemical reaction or dielectric interaction with the dyes mixed therewith.

DISCLOSURE OF THE INVENTION

45 [0005] Having noted the drawbacks in the prior art, we, the present inventors have assiduously studied, and, as a result, have found that a multi-layered, near-infrared-absorbing film or panel, which comprises an absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer material, solves the drawbacks. On the basis of this finding, we have completed the present invention. In addition, we have further found that the near-infrared-absorbing panel of such a multi-layered film or sheet of the invention that solves the drawbacks noted above is produced by a specific method of casting or coating a uniform mixture comprising a near-infrared-absorbing dye and a polymer resin. In
 50 the method, the dye and the polymer resin material may be selectively combined. These findings have augmented the completion of the invention. Accordingly, the object of the invention is to provide a film having a high near-infrared absorbance and a high visible-ray transmittance, and also a panel of a multi-layered sheet comprising the film.

Continuing
 55 [0006] The object of the invention is attained by a near-infrared-absorbing, single-layered or multi-layered film which comprises an absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer resin, and also by a multi-layered sheet panel comprising the film. When mixed with different dyes, some dyes change their characteristics, or some others chemically react with them or dielectrically interact with them, or still some others lose their thermal stability. Therefore, in the invention, individual dyes are separately sheeted into different films in suitable methods, depending on their characteristics, and a plurality of the resulting films are laminated to give a multi-layered film or sheet

*intr.
Polymer*

Dyes

in such a manner that the multi-layered film or sheet may exhibit desired color tones in the near-infrared-absorbing range and the visible-ray range.

[0007] The invention is described in detail hereinunder.

5 BEST MODES OF CARRYING OUT THE INVENTION

[0008] The film and the multi-layered sheet panel of the invention are a near-infrared-absorbing, single-layered or multi-layered film that comprises an absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer resin, and a near-infrared-absorbing, multi-layered sheet panel comprising the film, respectively.

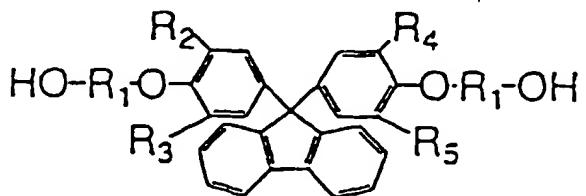
solvent [0009] The absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer resin, which is in the near-infrared-absorbing panel of the invention, may be any of a film as formed from a uniform solution of a near-infrared-absorbing dye and a polymer resin in a solvent through casting; a film as formed by applying a uniform solution of a near-infrared-absorbing dye and a polymer resin in a solvent onto a transparent film of polyester, polycarbonate or the like through coating; a film as formed through melt extrusion of a near-infrared-absorbing dye and a polymer resin; a film as formed by polymerizing and solidifying a uniform mixture of a near-infrared-absorbing dye and a monomer; or a film as formed through deposition of a near-infrared-absorbing dye along with a metal, a metal oxide or a metal salt on a transparent plastic film. Any one or more of these film layers may be in the panel, either singly or as combined. Specifically, different films of different near-infrared-absorbing dyes are formed in different methods, depending on the characteristics of the dyes, and a plurality of those films are laminated together, or the films are used singly. In that manner, the single-layered or multi-layered films may exhibit any desired color tones in the near-infrared-absorbing range and in the visible-ray range, in accordance with their objects.

[0010] In ordinary hot melt extrusion methods, films are generally formed at high temperatures not lower than 200°C. However, the film for the absorbing layer in the near-infrared-absorbing panel of the invention is formed in a casting method or a coating method, it may be dried in a mild condition at temperatures not higher than 150°C, at which the near-infrared-absorbing dyes used are not thermally decomposed. Therefore, in the method for the invention, even dyes having low heat resistance could be used so far as they are uniformly dispersed in ordinary organic solvent. Accordingly, the invention is advantageous in that the latitude in selecting the usable dyes is broad.

[0011] In the casting or coating method for forming the films of the invention, used is a transparent polymer resin as the binder for the dyes to be in the films. The polymer resin may be any of known transparent plastics including, for example, copolymers, polymethyl methacrylates, polycarbonates, polystyrenes, amorphous polyolefins, polyisocyanates, polyallylates, triacetylcelluloses, etc. Where it is desired to obtain thin films having a thickness of not larger than 50 microns and having the intended near-infrared absorbing capabilities, the dyes to be in the films must be dissolved in the binder resin to have a high concentration of from 1 to 5% by weight (relative to the solid content of the resin), though depending on their types. However, stable dye solutions having such a high concentration could not be prepared, if ordinary binder resins such as polycarbonates, acrylic resins or the like are used. Even if the dye could be forcedly dissolved in such a binder resin, the resulting solution is unfavorable as being problematic in that the dye is unevenly distributed therein, or is precipitated to give a solid floating near the surface of the solution, or the solution is coagulated.

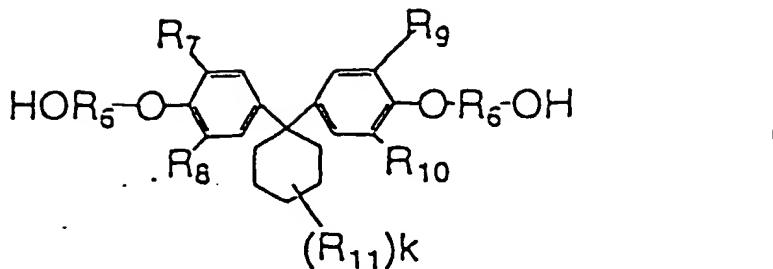
[0012] For the purpose of dissolving the dyes to give dye solutions having such a high concentration, preferred are the polyester resins described in the applicant's own JP-A Hei-06-184288, Hei-6-049186, Hei-07-149881, and Hei-08-100053. These polyester resins are preferred, as dissolving the dyes for use in the invention to form dye solutions having a high concentration. Accordingly, in the present invention, preferably used are the resins for the purpose of dissolving the dyes to give dye solutions having a high concentration.

[0013] The polyester resins are copolymerized with at least 10 mol% of an aromatic diol of any of the following general formulae (4) to (9):



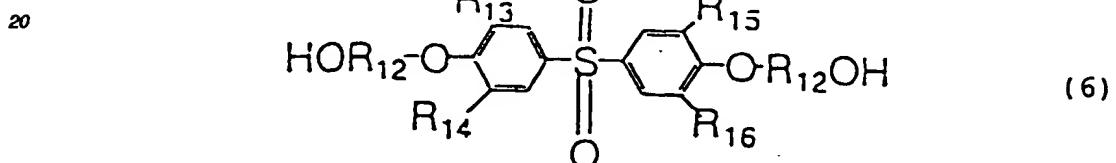
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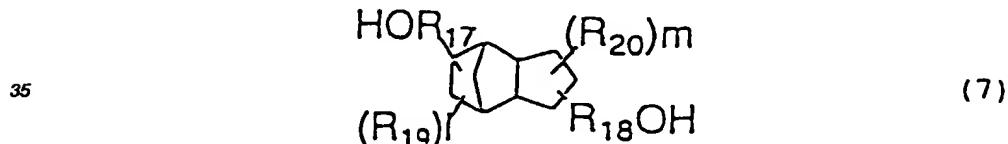
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wherein R₆ represents an alkylene group having from 1 to 4 carbon atoms; R₇, R₈, R₉, R₁₀ and R₁₁ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different; and k represents a natural number of from 1 to 4:

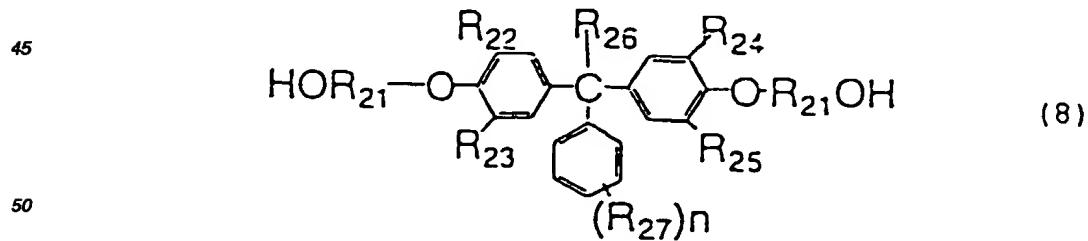


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wherein R₁₂ represents an alkylene group having from 1 to 4 carbon atoms; R₁₃, R₁₄, R₁₅ and R₁₆ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different:



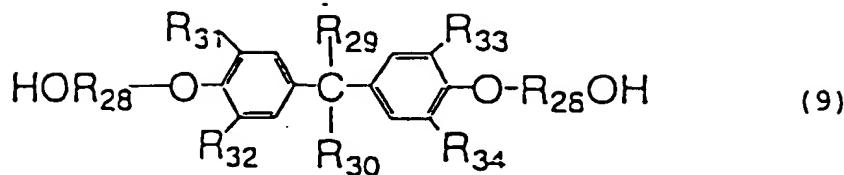
40 wherein R₁₇ and R₁₈ each represent an alkylene group having from 1 to 4 carbon atoms, and these may be the same or different; R₁₉ and R₂₀ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different; and l and m each represent a natural number of from 1 to 8:



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55 wherein R₂₁ represents an alkylene group having from 1 to 4 carbon atoms; R₂₂, R₂₃, R₂₄, R₂₅, R₂₆ and R₂₇ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different; and n represents a natural number of from 0 to 5:

5



10 wherein R₂₈ represents an alkylene group having from 1 to 4 carbon atoms; R₂₉ and R₃₀ each represent an alkyl group having from 1 to 10 carbon atoms, and these may be the same or different; R₃₁, R₃₂, R₃₃ and R₃₄ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different.

[0014] The compounds of formula (4) for the polyester polymers for use in the invention include, for example, 9,9-bis[4-(2-hydroxyethoxy)phenyl]-fluorene, 9,9-bis[4-(2-hydroxyethoxy)-3-methylphenyl]-fluorene, 9,9-bis[4-(2-hydroxyethoxy)-3,5-dimethylphenyl]-fluorene, 9,9-bis[4-(2-hydroxyethoxy)-3-ethylphenyl]-fluorene, 9,9-bis[4-(2-hydroxyethoxy)-3,5-diethylphenyl]-fluorene, etc. Of those, especially preferred is 9,9-bis[4-(2-hydroxyethoxy)phenyl]-fluorene, as giving polyester polymers having most balanced optical characteristics, heat resistance and shapability.

[0015] The compounds of formula (5) for the polyester polymers for use in the invention include, for example, 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3-methylphenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-dimethylphenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3-ethylphenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-diethylphenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3-propylphenyl]cyclohexane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-dibenzylphenyl]cyclohexane, etc.; and their derivatives in which from 1 to 4 hydrogens of the cyclohexane group are substituted with any of alkyl, aryl and aralkyl groups having from 1 to 7 carbon atoms. Of those, preferred is 1,1-bis[4-(2-hydroxyethoxy)phenyl]cyclohexane.

[0016] The compounds of formula (6) for the polyester polymers for use in the invention include, for example, bis-[4-(2-hydroxyethoxy)phenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3-methylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3,5-dimethylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3-ethylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3,5-diethylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3-propylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3,5-dipropylphenyl]-sulfone, bis-[4-(2-hydroxyethoxy)-3-isopropylphenyl]-sulfone, etc.

[0017] The compounds of formula (7) for the polyester polymers for use in the invention include, for example, tricyclodecanedimethylol, tricyclodecanediethylol, tricyclodecanedipropylol, tricyclodecanedibutylol, dimethyltricyclodecanedimethylol, diethyltricyclodecanedimethylol, diphenyltricyclodecanedimethylol, dibenzyltricyclodecanedimethylol, tetramethyltricyclodecanedimethylol, hexamethyltricyclodecanedimethylol, octamethyltricyclodecanedimethylol, etc. Of those, preferred is tricyclodecanedimethylol.

[0018] The dihydroxy compounds of formula (8) for the polyester polymers for use in the invention include, for example, 1,1-bis[4-(2-hydroxyethoxy)phenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3-methylphenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-dimethylphenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3-ethylphenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-diethylphenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3-propylphenyl]-1-phenylethane, 1,1-bis[4-(2-hydroxyethoxy)-3,5-dipropylphenyl]-1-phenylethane, etc.; and their derivatives in which the center carbon atom is substituted by any of alkyl, aryl and aralkyl groups having from 1 to 7 carbon atoms, and from 1 to 4 hydrogen atoms of the phenyl group of the side chain are substituted with any of alkyl, aryl and aralkyl groups having from 1 to 7 carbon atoms. Of those, preferred is 1,1-bis[4-(2-hydroxyethoxy)phenyl]-1-phenylethane.

[0019] The compounds of formula (9) for the polyester polymers for use in the invention include, for example, 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]butane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]pentane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3-methylbutane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]hexane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3-methylpentane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3,3-dimethylbutane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]heptane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3-methylhexane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]4-methylhexane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-5-methylhexane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3,3-dimethylpentane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3,4-dimethylpentane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-4,4-dimethylpentane, 2,2-bis[4-(2-hydroxyethoxy)phenyl]-3-ethylpentane, etc. Of those, especially preferred is 2,2-bis[4-(2-hydroxyethoxy)phenyl]-4-methylpentane, since the size of its branched side chain is large to a suitable degree and since the solubility in organic solvents of the polymers comprising it is high. In addition, the comonomer does not interfere with the heat resistance of the polymers comprising it. Also preferred is 2,2-bis[4-(2-hydroxyethoxy)phenyl]-propane, as having excellent heat resistance and mechanical strength. In addition, the comonomer does not interfere with the solubility in organic solvents of the polymers comprising it.

[0020] The diol compounds noted above may be employed either singly or as combined.

[0021] Any dicarboxylic acids that are employable for producing ordinary polyester resins may be used for producing

the polyester polymers for use in the invention. The dicarboxylic acids usable herein include, for example, aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,2-naphthalenedicarboxylic acid, 1,3-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 1,7-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 2,2'-biphenyldicarboxylic acid, 3,3'-biphenyldicarboxylic acid, 4,4'-biphenyldicarboxylic acid, etc.; aliphatic dicarboxylic acids such as malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, methylmalonic acid, ethylmalonic acid, methylsuccinic acid, 2,2-dimethylsuccinic acid, 2,3-dimethylsuccinic acid, 3-methylglutaric acid, 3,3-dimethylglutaric acid, etc.; alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, 2,5-dimethyl-1,4-cyclohexanedicarboxylic acid, 2,3,5,6-tetramethyl-1,4-cyclohexanedicarboxylic acid, etc. For the polymers that are required to have high heat resistance, especially preferred is 2,6-naphthalenedicarboxylic acid; and for those that are required to have good shapability, preferred is terephthalic acid. The dicarboxylic acids noted above can be employed herein either singly or as combined.

[0022] The polyester polymers for use in the invention can be produced in any known method of, for example, melt polymerization such as interesterification or direct polymerization, or of solution polycondensation, interfacial polymerization or the like. For the production, the reaction conditions including those for polymerization catalysts to be used may be any ordinary ones, for which any ordinary methods are employable.

[0023] Where the polyester polymers for use in the invention are produced through melt polymerization for interesterification, at least one or more compounds of the group of formulae (4) to (9) are used as comonomers, in which, preferably, the total amount of the dihydroxy compounds used is from 10 to 95 mol% of the diol component used. Where the total amount of the dihydroxy compounds is not smaller than 10 mol%, the solubility in organic solvents of the polymers produced could be high. Where it is not larger than 95 mol%, the melt polymerization is easy and the molecular weight of the polyester polymers to be produced can be well controlled to fall within a desired range. However, even if the total amount of the dihydroxy compounds used is larger than 95 mol%, the monomers could well be polymerized through solution polymerization or interfacial polymerization within a shortened period of time.

[0024] As the solvent for dissolving the resin and the dye in the invention, employable is any and every organic solvent of which the boiling point is acceptable in practical use, for example, it is not higher than 150°C. Popular solvents usable in the invention include, for example, aliphatic halides such as chloroform, methylene chloride, dichloromethane, dichloroethane, etc.; and non-halogen organic solvents such as toluene, xylene, hexane, methyl ethyl ketone, acetone, cyclohexane, etc.

[0025] For dissolving the resin and the dye in the invention, employed are any ordinary stirrers and kneaders. Where high-concentration solutions are prepared, butterfly mixers or planetary mixers may be employed, which, however, are not whatsoever limitative.

[0026] Where the film of the invention is produced from the solution having been prepared in the manner noted above, preferably employed is a casting or coating method. In the casting method, the solution is cast onto a glass sheet or a mirror-finished metal sheet, then spread on the surface of the sheet with a rod having grooves at regular intervals thereon, and then dried, and thereafter the film formed on the sheet is peeled off in any desired manner. Thus is obtained the intended finished film. Needless-to-say, the method may be automatically machined to obtain the film, for example, by using an ordinary casting machine.

[0027] In the coating method, in general, a film or panel is coated with the solution having been prepared in the manner noted above, which is then dried to form a film layer thereon. For example, where a transparent or other functional film is coated with the solution, any ordinary coating machine is employable. Using the machine, the film to be coated is moved at a speed of from a few meters/min to tens meters/min, while the solution is extruded through a T-die onto the moving film, and the thus-coated film is dried in the next drying zone where the solvent is removed, and thereafter the thus-dried film is wound up. In the machine, the series of this coating process is completed automatically.

[0028] The absorbing layer to be in the near-infrared-absorbing panel of the invention may be formed through melt extrusion, which has the advantage of easiness and inexpensiveness in forming the layer. In this case, in general, the resin and the dye are fed into a single-screw or double-screw kneader via a feeder, melted and kneaded therein at a predetermined temperature, generally at around 300°C, and then extruded out through a T-die to give a film. Needless-to-say, the invention is not limited to the general melt extrusion.

[0029] As the absorbing layer to be in the near-infrared-absorbing panel of the invention, also employable is a film formed through polymerization and solidification. As monomers in this case, usable are any known vinyl compounds such as styrene, butadiene, isoprene, methyl acrylate, etc. The dye may be previously kneaded with the monomers along with an initiator to give a uniform liquid mixture. The dye-containing monomer mixture is cast into a frame made of sheet glass or the like, and is heated or is exposed to ultraviolet rays, whereby the monomers are polymerized.

[0030] Accordingly, for example, where dyes having poor heat resistance are used in forming the absorbing layer to be in the near-infrared-absorbing panel of the invention, the film of the layer may be formed according to the casting method; where those having poor dispersibility are used, the film of the layer may be formed according to the method of polymerization followed by solidification; and where any other dyes are used, the film of the layer may be formed

✓

Remanj
solvent.

according to the melt extrusion method. A plurality of the films thus produced may be laminated to form the panel of the invention, in which, therefore, any desired dyes can be used for forming the individual films with no limitation. The dye density of each film layer can be separately controlled, and the color tone of the panel constituting the plural film layers may be any desired one.

5 [0031] The especially important characteristics of near-infrared-absorbing panels are the absorbability for near-infrared rays, concretely those falling within a wavelength range of from 850 nm to 1200 nm, the transmittance for visible rays, concretely those falling within a wavelength range of from 400 nm to 800 nm, and the color tone.

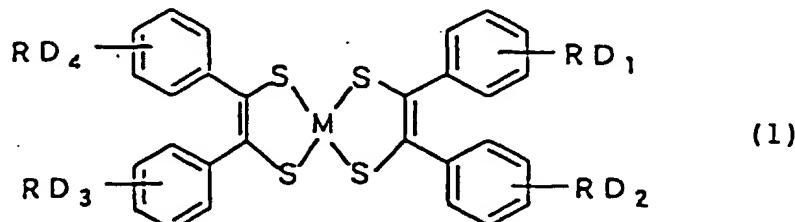
[0032] Of those characteristics, the near-infrared absorbability is the most important. In some uses, however, the other two characteristics are extremely important. For example, for near-infrared-absorbing panels which are for absorbing near-infrared rays from image output devices, thereby preventing the malfunction of remote controllers that operate in a near-infrared range, not only the transmittance within a visible ray range but also the color tone is extremely important especially when they are used for color image output devices. Specifically, the color difference in full color must be minimized as much as possible in the panels. Concretely, the panel must have gray or brown color tone. In that case, plural dyes must be delicately combined to produce the intended color tone of the panels.

10 [0033] For producing near-infrared-absorbing panels according to conventional techniques, employed was a method of kneading a transparent polymer resin and a near-infrared absorbing dye followed by extruding the resulting mixture into a sheet through hot melt extrusion, or a method of polymerizing monomers along with a near-infrared dye. In those conventional methods, however, only dyes which are not decomposed under heat could be used, and the latitude in selecting the desired dyes is narrow. In those, therefore, it is extremely difficult to obtain panels having the characteristics noted above.

15 [0034] As opposed to those produced according to the conventional methods, the near-infrared-absorbing panels of the invention are advantageous in that they can use the films formed in a casting or coating method, in which even dyes having poor heat resistance can be used. Therefore, for the panels of the invention, the latitude in selecting the desired dyes is broad.

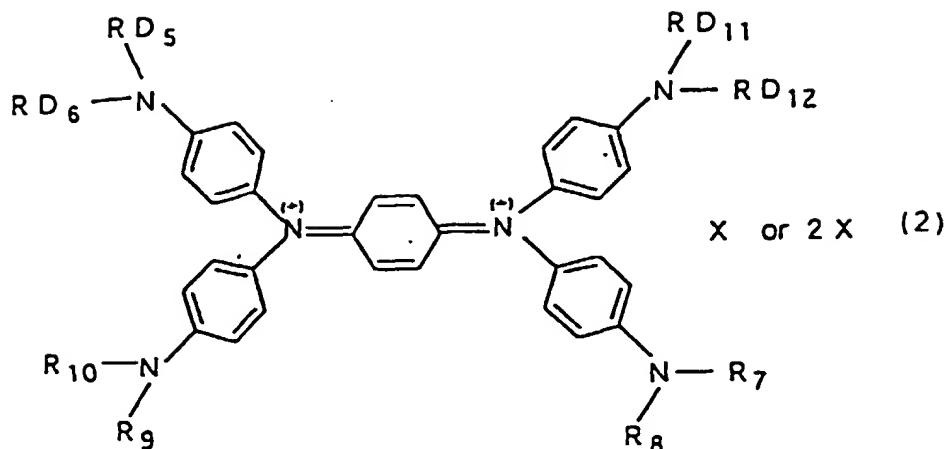
20 [0035] Any and every dye having near-infrared absorbability is usable in forming the absorbing layer to be in the near-infrared-absorbing panel of the invention. For example, the dyes usable in the invention include polymethine dyes (cyanine dyes), phthalocyanine dyes, naphthalocyanine dyes, dithiol-metal complex dyes, naphthoquinone dyes, anthroquinone dyes, triphenylmethane dyes, aminium (or aluminium) dyes, di-immonium dyes, etc.

25 [0036] Of those, preferably combined are at least two or more of three different types of dyes, aromatic dithiol-metal complexes or a general formula (1):

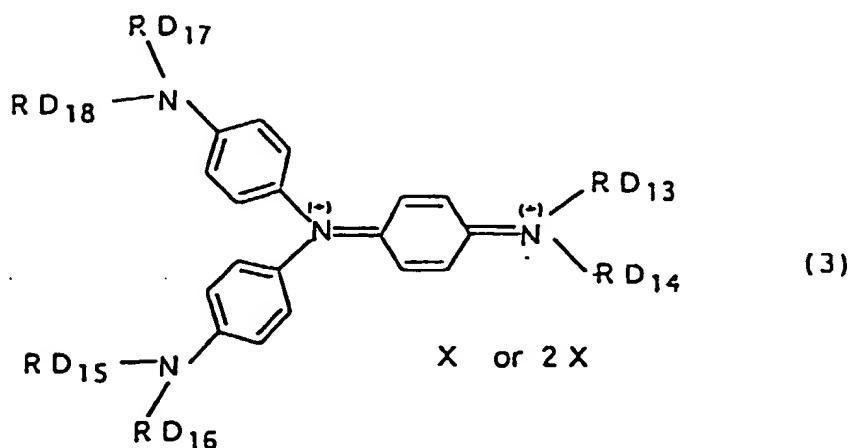


45 wherein R₁ and R₂ each represent an alkylene group having from 1 to 4 carbon atoms, an aryl group, an aralkyl group, a fluorine atom or a hydrogen atom; and M represents a tetradentate transition metal,

aromatic di-immonium compounds of general formula (2) or (3):



20 wherein R₁ to R₈ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a monovalent anion,

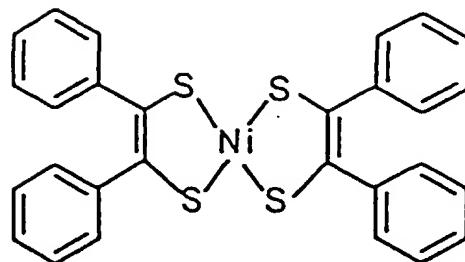


45 wherein R₁ to R₈ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a monovalent anion,

and phthalocyanine dyes. The combination is one novel aspect of the invention.

[0037] The aromatic dithiol-metal complexes noted above include, for example, nickel bis-1,2-diphenyl-1,2-ethenedithiolate, and its derivatives in which one hydrogen of the two aromatic rings is substituted with a substituent of any of an alkylene group having from 1 to 4 carbon atoms, an aryl group, an aralkyl group or a fluorine atom. Concretely mentioned are compounds of the following chemical formulae (10) and (11), which, however, are not whatsoever limitative.

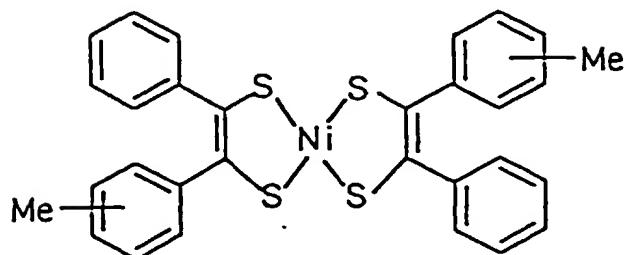
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(10)

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(11)

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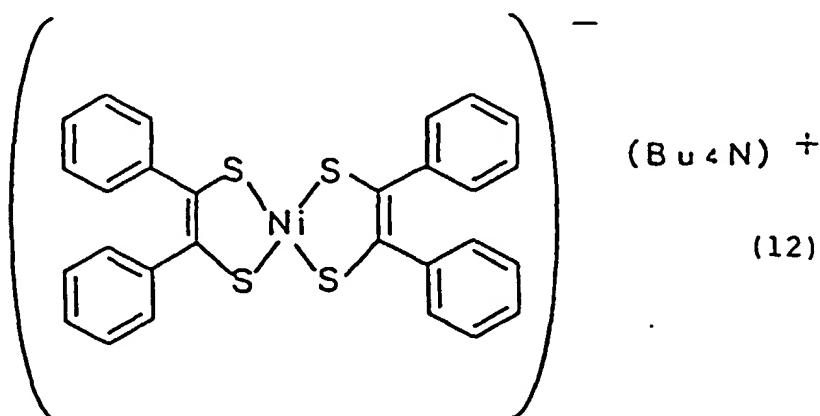
30 [0038] In addition, ionized derivatives of the compounds noted above, such as a compound of the following chemical formula (12), are also employable. Needless-to-say, those compounds specifically mentioned herein are not limitative. In the ionized compounds, the counter ion may be any and every monovalent cation except tetrabutylammonium ion used in the chemical formula (12). For example, the cations described in literature, "Development of Functional Dyes, and Market Trends" (by CMC Publishing) are acceptable.

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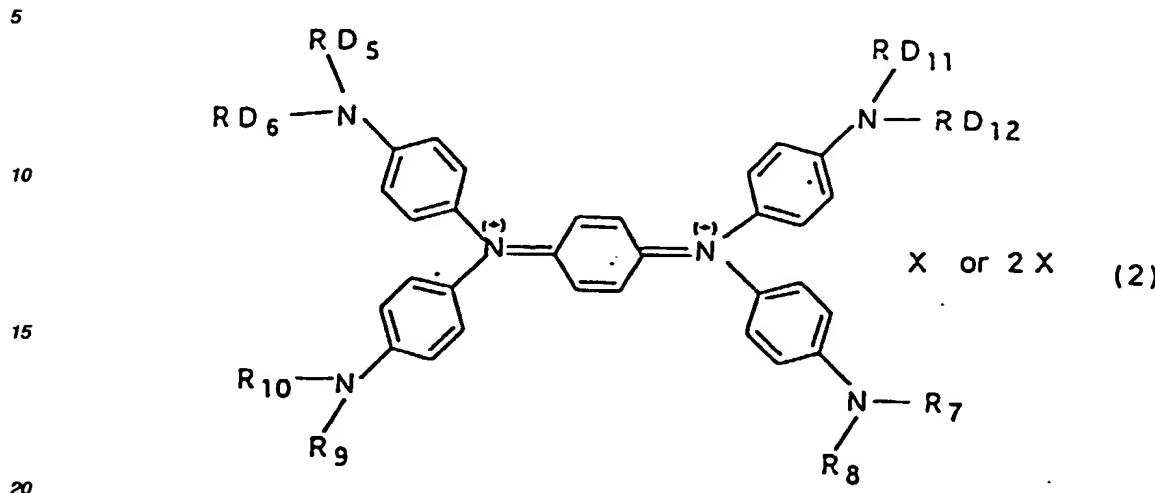


(12)

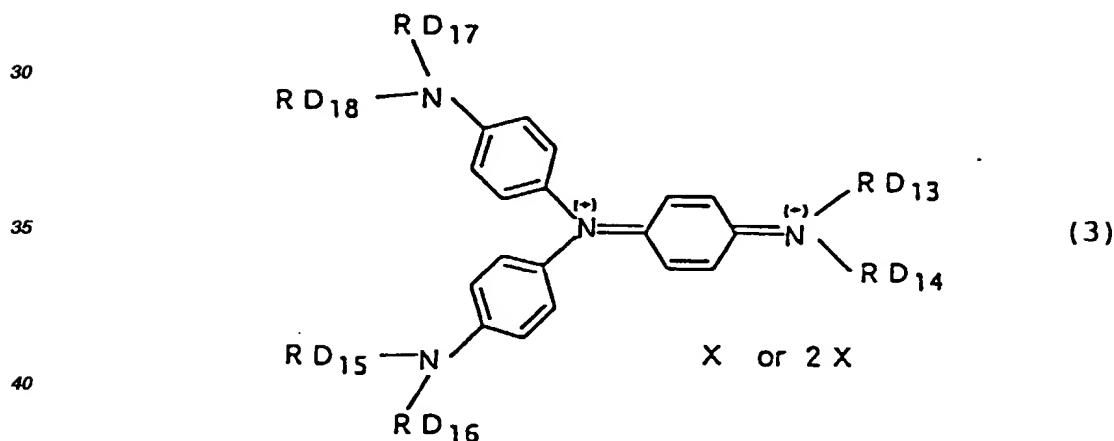
55 [0039] In place of the metallic nickel, any and every tetravalent transition metal is employable, which includes, for example, titanium, vanadium, zirconium, chromium, molybdenum, ruthenium, osmium, cobalt, platinum, palladium, etc. [0040] The dyes strongly absorb the rays falling within a wavelength range of from 850 to 900 nanometers (nm). As cutting off near-infrared rays that are applied to remote controllers, etc., the dyes are effective for preventing remote controllers from malfunctioning. When laminated with an electromagnetic radiation-absorbing layer of so-called low-

radiation glass, ITO or IXO, which will be described in detail hereinunder, to produce multi-layered panels, the dye layer in the panels produced more effectively cuts off near-infrared rays.

[0041] The aromatic di-immonium compounds of formulae (2) and (3):

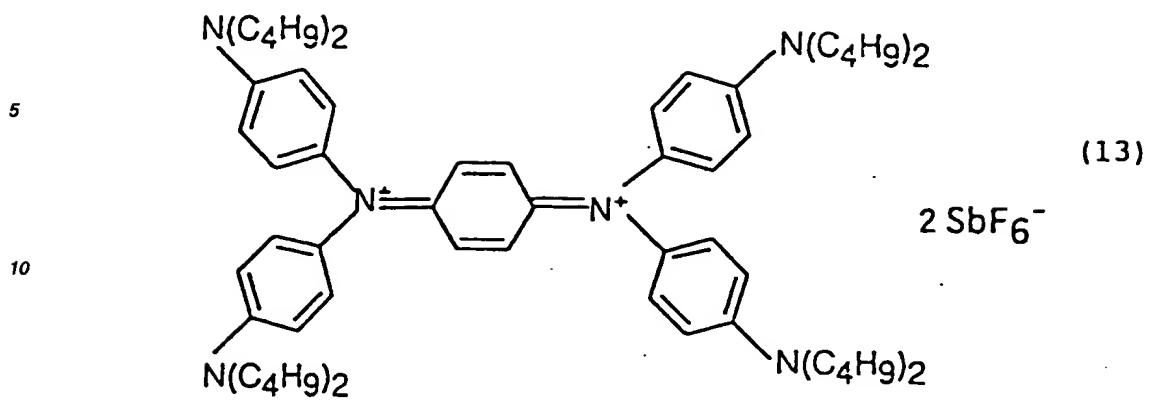


25 wherein R₁ to R₈ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a monovalent anion,

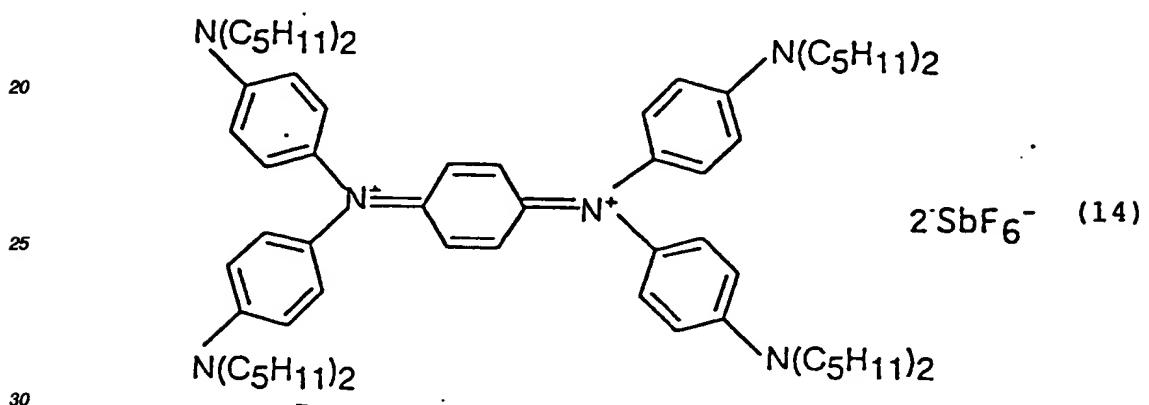


45 wherein R₁ to R₈ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a monovalent anion,

50 include, for example, compounds of the following chemical formulae (13) to (17), which, however, are not whatsoever limitative. Except the hexafluoroantimonate ion in the compounds illustrated, any other monovalent anions are employable. Preferred examples of the anions include hexafluorophosphate ion, tetrafluoroborate ion, perchlorate ion, etc.



$2 SbF_6^-$



$2 SbF_6^-$

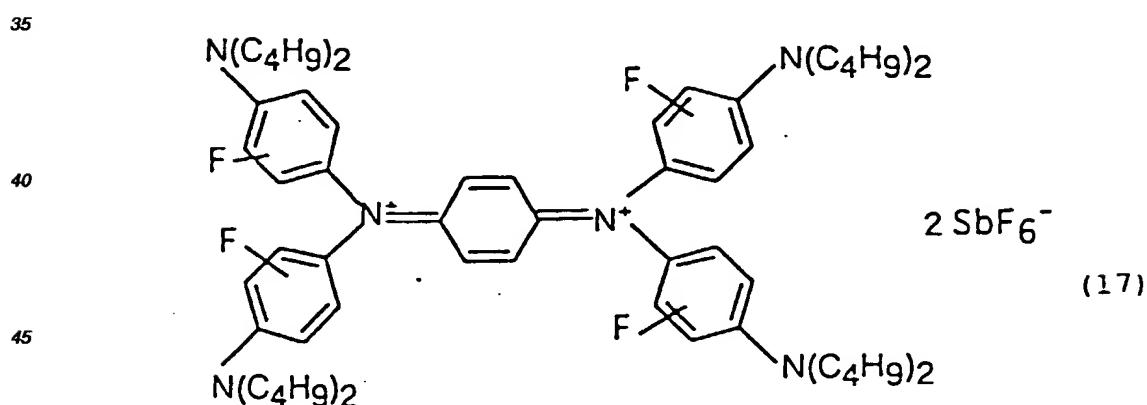
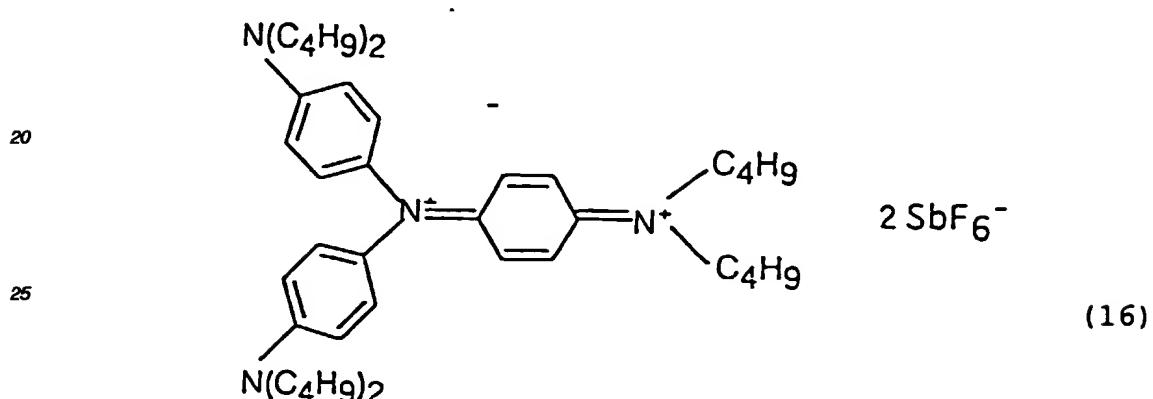
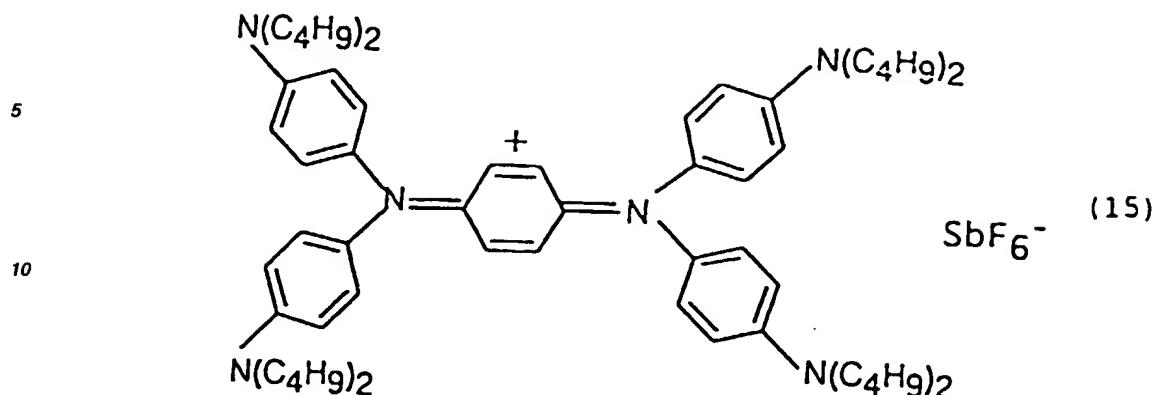
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50 [0042] The dyes strongly absorb the rays at around 1000 nm. As cutting off not only near-infrared rays that are applied to remote controllers and the like but also rays to be applied to computer communication systems which will be widely used in future, the dyes are effective for preventing the systems from malfunctioning. When laminated with a meshed or etched electromagnetic radiation-absorbing layer, which will be described in detail hereinunder, to produce multi-layered panels, the dye layer is more effective.

55 [0043] The above-mentioned two types of dyes (aromatic dithiol-metal complexes, and aromatic di-immonium compounds) are especially effective. Where the dyes of those types have the ability to absorb visible rays, they may be combined with color tone-correcting dyes to modulate the color tone of the panels comprising them. As the color tone-

correcting dyes for that purpose, effectively used are phthalocyanine dyes. Any and every phthalocyanine dye is employable herein, for example, those described in literature, "Development of Functional Dyes, and Market Trends" (by CMC).

[0044] In general, the near-infrared-absorbing, aromatic di-immonium dyes mentioned above are unstable to heat. Therefore, if the dye layer is formed through melt extrusion or through polymerization followed by solidification, the dyes will be thermally decomposed, resulting in that the near-infrared absorbability of the dye layer will be poor. Accordingly, when the dyes are used in the absorbing layer, it is especially desirable that the dye-containing absorbing layer is formed in a casting method.

[0045] For producing the near-infrared-absorbing panel of the invention, previously shaped sheets or films must be laminated in any suitable method. For the lamination, preferably used is a powerful, transparent polymer adhesive. The polymer adhesive of that type includes, for example, two-liquid epoxy adhesives, unsaturated polyester adhesives, urethane adhesives, phenolic resin adhesives, vinyl resin adhesives, and acrylic adhesives.

[0046] The near-infrared-absorbing panel of such a multi-layered film or sheet of the invention may have only the near-infrared-absorbing layer noted above as the layer having a specific function. Preferably, however, the multi-layered film or sheet of the panel additionally has any other functional layers, such as an electromagnetic radiation-absorbing layer, an antireflection layer, a shape-retaining layer, etc., in addition to the absorbing layer. The electromagnetic radiation-absorbing layer is a transparent conductive film, for which preferred are polyester films, glass sheets, acrylic sheets or polycarbonate sheets coated with a thin deposit of a metal, metal oxide, metal salt or the like. Conductive films having a lower sheet resistivity may have higher electromagnetic radiation absorbability, but on the other hand, the thickness of the metallic deposit layer to be formed on them shall be larger, resulting in that the light transmittance of such thick films is lowered. The antireflection layer is to prevent surface reflection on the panel, while increasing the light transmittance of the panel and preventing the panel from "glaring".

[0047] In the present invention, preferably used are metal-deposited polyester films, glass sheets, acrylic sheets or polycarbonate sheets as the electromagnetic radiation-absorbing layer in the panel, which, however, are not whatsoever limitative. A film as meshwise coated with a conductive material through screen-printing or the like may also be used as the electromagnetic radiation-absorbing layer. As the case may be, a single, metal-deposited film that acts both as the antireflection layer and as the electromagnetic radiation-absorbing layer may be used. In that case, the metal-deposited film is the outermost layer of the panel. The function of the shape-retaining layer is to retain the overall shape of the panel in which the near-infrared-absorbing layer has low mechanical strength and could hardly retain its shape. In addition, the shape-retaining layer further acts to increase the heat resistance of the entire panel and to increase the abrasion resistance of the surface of the panel. Any transparent resin or glass is preferably used as the material for the shape-retaining layer. In general, preferred are polycarbonates, polyacrylonitriles, polymethyl methacrylates, polystyrenes, and polyesters. Especially preferred are polycarbonates in view of their heat resistance, and polymethyl methacrylates in view of their transparency and abrasion resistance. Glass is also preferred for increasing the mechanical strength and the heat resistance of the panel.

[0048] As the electromagnetic radiation-shielding, transparent conductive layer noted above, employable is a so-called heat-reflecting glass sheet as prepared by coating a glass substrate with three or more layers of transparent dielectric film/thin metal film/transparent dielectric film through vapor deposition. The glass sheet of that type is widely used as exteriors or windowpanes of buildings, and as windshields for cars and aircraft. As the transparent dielectrics to be used in this, preferred are titanium oxide, zirconia oxide, hafnium oxide, bismuth oxide, etc. As the thin metal film, preferred are gold, platinum, silver, and copper. In place of the thin metal film, also preferably used is any of titanium nitride, zirconia nitride, or hafnium nitride.

[0049] The electromagnetic radiation-shielding, transparent conductive layer may be further coated with a transparent, conductive oxide film. As the oxide for the film, preferably used are fluorine-doped tin oxide, tin-doped indium trioxide, aluminium-doped zinc oxide, etc.

[0050] Where the metal-deposited layer is used as the electromagnetic radiation-shielding, transparent conductive layer, it must be combined with a near-infrared-absorbing film suitable to it. For example, heat-reflecting glass absorbs rays having a wavelength longer than 1200 nanometers. Therefore, the dyes in the near-infrared-absorbing film to be combined with the heat-reflecting glass sheet shall absorb rays not falling within the wavelength range of the rays to be absorbed by the heat-reflecting glass sheet. Needless-to-say, heat-reflecting glass sheets have different absorption characteristics, depending on the materials constituting them. Therefore, by controlling the dyes to be combined and also their concentration in the near-infrared-absorbing film, the film must be so modulated as to be suitable to the glass sheet to be combined therewith. For this purpose, used are the aromatic dithiol-metal complexes of the dyes mentioned hereinabove, preferably the aromatic dithiol-nickel complexes, most preferably nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, or its derivative in which the hydrogen of the benzene ring is substituted with a fluorine atom or a methyl group. For further modulating the color tone of the dye-containing layer, a phthalocyanine dye may be added thereto.

[0051] Where the electromagnetic radiation-shielding conductive layer has near-infrared-reflecting capabilities and where it is combined with a near-infrared-absorbing film of the invention that contains, in a transparent polymer resin,

Silver

[0051]

a % by weight, relative to the resin, of a dithiol-metal complex, b % by weight of a phthalocyanine dye, c % by weight of a di-immonium dye and d % by weight of an aminium dye, the ranges within which the dyes act effectively are $0.1 \leq a \leq 5.0$, $0.01 \leq b \leq 2.0$, $0.1 \leq c \leq 3.0$, and $0.01 \leq d \leq 1.0$, preferably $0.5 \leq a \leq 2.5$, $0.01 \leq b \leq 2.0$, $0.2 \leq c \leq 1.0$, and $0.1 \leq d \leq 0.5$. Specifically, the dyes to be in the absorbing layer are preferably so formulated that they satisfy the requirement of $0.81 \leq a + b + c + d \leq 6.0$. The resin mixture comprising the dyes noted above is sheeted into a film of the absorbing layer through casting, coating, melt extrusion or polymerization. In the polymerization method, the dyes are added to the monomers to be polymerized. If, however, the dyes are formulated under the condition of $a + b + c + d < 0.81$ and the resin mixture comprising them is sheeted into a film, the resulting film has poor near-infrared absorbability though it may have a high degree of visible ray transmittance. The film, even if used in near-infrared radiation-shielding filters, is no more effective and is unfavorable. On the other hand, if the dyes are formulated under the condition of $a + b + c + d > 6.0$ and the resin mixture comprising them is sheeted into a film, the resulting film has a low degree of visible ray transmittance though it may have good near-infrared absorbability. The film is useless in optical filters. Regarding these matters, one preferable embodiment is shown in Example 24 mentioned below, and one nonpreferable embodiment is in Comparative Example 1.

[0052] Where the electromagnetic radiation-shielding, transparent conductive layer is a mesh-type one, such as that mentioned above, and where it is combined with a near-infrared-absorbing film of the invention, the absorption of the rays falling within an intended wavelength range must be attained by the dyes only that exist in the absorbing film, since the mesh-type layer has no near-infrared absorbability. The same shall apply to the layer not having electromagnetic radiation shieldability. As the dyes for that purpose, preferred is a mixture of an aromatic di-immonium compound and an aromatic dithiol-metal complex. Like in the above, the aromatic dithiol-metal complex is preferably an aromatic dithiol-nickel complex, most preferably nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, or its derivative in which the hydrogen of the benzene ring is substituted with a fluorine atom or a methyl group. In the aromatic di-immonium compound, the counter anion is preferably a hexafluoroantimonate, hexafluoroarsenate, perchlorate or tetrafluoroborate ion. If desired, a phthalocyanine dye may be added to the dye mixture for color modulation.

[0053] Where the electromagnetic radiation-shielding conductive layer does not have near-infrared-reflecting capabilities, and where it is combined with a near-infrared-absorbing of the invention that contains, in a transparent polymer resin, a % by weight, relative to the resin, of a dithiol-metal complex, b % by weight of a phthalocyanine dye, c % by weight of a di-immonium dye and d % by weight of an aminium dye, as in the above, the preferred ranges for the dyes are $0.1 \leq a \leq 3.0$, $0.01 \leq b \leq 2.0$, and $0.1 \leq c \leq 5.0$, more preferably $0.5 \leq a \leq 2.0$, $0.1 \leq b \leq 1.0$, and $1.0 \leq c \leq 3.0$. Specifically, the dyes to be in the absorbing layer are preferably so formulated that they satisfy the requirement of $1.6 \leq a + b + c \leq 6.0$. The resin mixture comprising the dyes noted above is sheeted into a film of the absorbing layer through casting, coating, melt extrusion or polymerization. In the polymerization method, the dyes are added to the monomers to be polymerized. If, however, the dyes are formulated under the condition of $a + b + c < 1.6$ not satisfying the requirement noted above and the resin mixture comprising them is sheeted into a film, the resulting film has poor near-infrared absorbability though it may have a high degree of visible ray transmittance. The film, even if used in near-infrared radiation-shielding filters, is no more effective and is unfavorable. On the other hand, if the dyes are formulated under the condition of $a + b + c > 6.0$ and the resin mixture comprising them is sheeted into a film, the resulting film has a low degree of visible ray transmittance though it may have good near-infrared absorbability. The film is useless in optical filters. Regarding these matters, one preferable embodiment is shown in Example 25 mentioned below, and one nonpreferable embodiment is in Comparative Example 3.

[0054] Embodiments of the present invention are described concretely with reference to Fig. 1.

[0055] In Fig. 1, 1 is an antireflection layer; 2 is a shape-retaining layer of a transparent resin such as polycarbonate, polymethyl methacrylate or the like or of glass; 3 is a transparent conductive layer that acts as an electromagnetic radiation-shielding layer and also as a near-infrared radiation-shielding layer, and this is formed on a polyester film through vapor deposition, or is directly deposited on a glass sheet. 4 is a near-infrared-absorbing layer of a dye having poor heat resistance or a dye having poor dispersibility, and this is formed through coating or casting. 5 is a layer having both near-infrared absorbability and shape retainability, and this is formed through melt extrusion or polymerization of monomers followed by solidification.

[0056] As illustrated, a plurality of layers having different properties are laminated in different manners mentioned below to form various multi-layered structures of typical embodiments of the invention. However, the invention is not whatsoever limited to the illustrated ones, but encompasses any and every combination that indispensably contains the near-infrared-absorbing layer.

[0057] Fig. 1-A illustrates one embodiment of the invention, in which the antireflection layer 1 is attached to one surface of the shape-retaining layer 2 of polycarbonate, polymethyl methacrylate, glass or the like, while the transparent conductive layer 3 and the near-infrared-absorbing layer 4 are laminated on the other surface of the layer 2 in that order. The layer 4 is formed through coating or casting.

[0058] Fig. 1-B illustrates another embodiment of the invention, in which the antireflection layer 1 is attached to one surface of the shape-retaining layer 2 of polycarbonate, polymethyl methacrylate, glass or the like, while the transparent

conductive layer 3 and the near-infrared-absorbing layer 4 are laminated on the other surface of the layer 2 in that order, and in which another shape-retaining 2 of polycarbonate, polymethyl methacrylate, glass or the like is laminated on the layer 4. The layer 4 is formed through coating or casting.

[0059] Fig. 1-C illustrates still another embodiment of the invention, which is a laminate composed of the antireflection layer 1, the transparent conductive layer 3, and the panel layer 5 having both near-infrared absorbability and shape retainability. The layer 5 is formed through melt extrusion or polymerization of monomers followed by solidification.

[0060] The advantages and the novelty of the invention are described concretely with reference to the following Examples.

[0061] In Examples, the near-infrared absorbability, the visible ray transmittance and the color tone of each sample produced are measured and evaluated according to the methods mentioned below.

(1) Near-Infrared Absorbability:

[0062] Of each panel produced in Examples, the light transmittance for the wavelength range falling between 900 nm and 1200 nm was measured, using a spectrophotometer (Best-570, manufactured by Nippon Bunko KK), and the mean value, T % was obtained. From this, obtained was the near-infrared cut-off percentage (%) of each panel, which is represented by (100 - T). Each panel is evaluated on the basis of the percentage thus obtained.

(2) Visible Ray Transmittance:

[0063] Using the same spectrophotometer as in (1), the mean light transmittance, T_v % for the wavelength range falling between 450 nm and 700 nm was measured, which indicates the visible ray transmittance of each panel.

Example 1:

[0064] Starting compounds of 0.4 mols of dimethyl terephthalate (DMT), 0.88 mols of ethylene glycol (EG) and 0.28 mols of 9,9-bis(4-(2-hydroxyethoxy)phenyl)fluorene (BPEF) were polymerized through ordinary melt polymerization to give a fluorene copolyester (DM/BPEF = 3/7, by mol). The copolyester had a limiting viscosity $[\eta]$ of 0.42, a molecular weight M_w of 45,000, and a glass transition point T_g of 140°C.

[0065] Nickel bis-1,2-diphenyl-1,2-ethene-dithiolate was produced according to a known method (Harry B. Gray, et al., *J. Am. Chem. Soc.*, Vol. 88, pp. 43-50, pp. 4870-4875, 1966), and purified through recrystallization to have a purity of not lower than 99 %.

[0066] The fluorene copolyester was dispersed and dissolved in methylene chloride along with 0.038 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, 0.005 % by weight of phthalocyanine dye (EX Color 801K, manufactured by Nippon Shokubai), and 0.005 % by weight of phthalocyanine dye (EX Color 802K, manufactured by Nippon Shokubai), and the resulting dye dispersion was cast to form a film having a thickness of 150 μm .

Example 2:

[0067] Using an epoxy adhesive, the film formed in Example 1 was sandwiched between polymethyl methacrylate substrates of 1 mm thick, of which one surface was laminated with a film of 100 μm thick that had been prepared by depositing a near-infrared-absorbing and electromagnetic radiation-absorbing layer of silver complex [ITO/(silver + platinum)/ITO - this indicates a structure of (silver + platinum) as sandwiched between ITO (indium tin oxide)] on a transparent polyester. Thus was produced a near-infrared-absorbing panel having the structure of Fig. 1-A, and its characteristics were evaluated. The spectral transmittance curve of this panel is shown in Fig. 2. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 70 %. The panel was good.

Example 3:

[0068] In the same manner as in Example 1 except that triacetetyl cellulose (LT-35, manufactured by Daicel Chemical) was used as the casting polymer, a near-infrared-absorbing panel having the structure of Fig. 1-A was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 70 %. The panel was good.

Example 4:

[0069] 0.005 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, 0.001 % by weight of phthalocyanine dye

(EX Color 801K, manufactured by Nippon Shokubai), and 0.001 % by weight of phthalocyanine dye (EX Color 802K, manufactured by Nippon Shokubai) were dispersed in polymethyl methacrylate, and sheeted into a film having a thickness of 2 mm through melt extrusion.

[0070] One surface of this film was laminated with a film (thickness: 100 µm) that had been prepared by depositing a near-infrared-absorbing and electromagnetic radiation-absorbing layer of silver complex [ITO/(silver+platinum)/ITO] on a transparent polyester. Thus was produced a near-infrared-absorbing panel having the structure of Fig. 1-C, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 65 %. The panel was good.

10 Example 5:

[0071] 0.005 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, 0.02 % by weight of aminium dye of formula (16), 0.01 % by weight of phthalocyanine dye (EX Color 801K, manufactured by Nippon Shokubai), and 0.01 % by weight of phthalocyanine dye (EX Color 802K, manufactured by Nippon Shokubai) were dispersed in polymethyl methacrylate, and sheeted into a film having a thickness of 2 mm through melt extrusion.

[0072] The film thus prepared herein, and a film (thickness: 100 µm) that had been prepared by depositing an electromagnetic radiation-absorbing layer of silver complex [ITO/(silver + platinum)/ITO] on a transparent polyester were laminated on a shape-retaining layer. Thus was produced a near-infrared-absorbing panel having the structure of Fig. 1-A, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 64 %. The panel was good.

Example 6:

[0073] 0.005 % by weight of di-immonium dye of formula (13) and 0.001 % by weight of phthalocyanine dye (EX color 803K, manufactured by Nippon Shokubai) were dispersed in polymethyl methacrylate, and sheeted into a film having a thickness of 2 mm through melt extrusion.

[0074] The film thus prepared herein, and a film (thickness: 100 µm) that had been prepared by depositing an electromagnetic radiation-shielding layer of silver complex [(gold + silver)/ITO - this indicates a structure composed of ITO and (silver + platinum)] on a transparent polyester were laminated on a shape-retaining layer. Thus was produced a near-infrared-absorbing panel having the structure of Fig. 1-C, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 65 %. The panel was good.

Example 7:

[0075] The fluorene copolyester prepared in Example 1 was mixed with 0.1 % by weight, relative to the copolyester, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.03 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) in chloroform, and the resulting mixture was dried at room temperature and then at 70°C to form a film having a thickness of 150 µm.

[0076] An electromagnetic radiation-shielding film of 200 µm thick that had been prepared by depositing silver complex [(gold + silver)/ITO] on a polyester film, a "non-glare" and antireflection film, and the near-infrared-absorbing film prepared herein were laminated on an acrylic sheet having a thickness of 3 mm to produce a near-infrared-absorbing panel having the structure of Fig. 1-A, and the characteristics of the panel were evaluated. The spectral transmittance curve of this panel is shown in Fig. 3. The near-infrared cut-off percentage of this panel was 95 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 8:

[0077] In the same manner as in Example 7 except that 0.1 % by weight, relative to the fluorene copolyester obtained in Example 1, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.05 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 95 %, and the visible ray transmittance thereof was 62 %. The panel was good.

Example 9:

55 Example 9:

[0078] In the same manner as in Example 7 except that 0.15 % by weight, relative to the fluorene copolyester obtained in Example 1, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.03 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used,

a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 10:

[0079] In the same manner as in Example 7 except that 0.15 % by weight, relative to the fluorene copolyester obtained in Example 1, of di-immonium compound dye of formula (13) and 0.05 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 11:

[0080] In the same manner as in Example 7 except that triacetyl cellulose was used as the casting polymer and that 0.1 % by weight, relative to triacetyl cellulose, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.03 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 63 %. The panel was good.

Example 12:

[0081] In the same manner as in Example 7 except that triacetyl cellulose was used as the casting polymer and that 0.1 % by weight, relative to triacetyl cellulose, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.05 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 13:

[0082] In the same manner as in Example 7 except that triacetyl cellulose was used as the casting polymer and that 0.15 % by weight, relative to triacetyl cellulose, of di-immonium compound dye of formula (13), 0.05 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.03 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 63 %. The panel was good.

Example 14:

[0083] In the same manner as in Example 7 except that triacetyl cellulose was used as the casting polymer and that 0.15 % by weight, relative to triacetyl cellulose, of di-immonium compound dye of formula (13) and 0.05 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 95 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 15:

[0084] In the fluorene copolyester that had been prepared in Example 1, dispersed were 0.225 % by weight, relative to the copolyester, of di-immonium dye of formula (13), 0.075 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.045 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai), and an adhesive polyester film (manufactured by Dia Foil) was coated with the resulting dispersion and dried. The resulting film had a thickness of 50 µm.

[0085] Apart from the film of 50 µm thick prepared above, further prepared were an electromagnetic radiation-shielding film (thickness: 50 µm) having a deposit layer of silver complex [IDIXO (manufactured by Idemitsu Kosan)/silver/IDIXO - this indicates a structure of silver as sandwiched between IDIXO] formed on a polyester film, and an antireflection film, and a shape-retaining substrate of glass having a thickness of 3 mm. Next, the electromagnetic radiation-shielding film was attached onto the both surfaces of the shape-retaining substrate in such a manner that elec-

trodes could be mounted on the resulting laminate, and the near-infrared-absorbing film prepared herein was further attached onto one surface of the laminate. Finally, the antireflection film was attached onto the both surfaces of the laminate. Thus was produced a near-infrared-absorbing, electromagnetic radiation-shielding panel having the structure of Fig. 1-A, and its characteristics were evaluated. The spectral transmittance curve of this panel is shown in Fig. 4. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 16:

[0086] In the same manner as in Example 15 except that a polymethyl methacrylate sheet having a thickness of 3 mm was used as the shape-retaining substrate, a near-infrared-absorbing, electromagnetic radiation-shielding panel was produced. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 17:

[0087] In the same manner as in Example 15 except that a polycarbonate sheet having a thickness of 3 mm was used as the shape-retaining substrate, a near-infrared-absorbing, electromagnetic radiation-shielding panel was produced. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 18:

[0088] In the same manner as in Example 15 except that 0.2 % by weight, relative to the fluorene copolyester obtained in Example 1, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.08 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing, electromagnetic radiation-shielding panel was produced, and its characteristics were evaluated. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 19:

[0089] In the same manner as in Example 14 except that butyral resin (Denka Butyral 6000E, manufactured by Nippon Denka Kogyo) was used as the transparent polymer resin for the near-infrared-absorbing film and that methyl ethyl ketone was used as the solvent for dispersing the resin and the dyes, a near-infrared-absorbing, electromagnetic radiation-shielding panel was produced. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

Example 20:

[0090] In the fluorene copolyester that had been prepared in Example 1, dispersed were 0.45 % by weight, relative to the copolyester, of di-immonium dye of formula (13), 0.12 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.06 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai). An adhesive polyester film substrate (A4100, manufactured by Toyobo) was coated with the resulting dispersion, and dried. Thus was produced a near-infrared-absorbing filter, which had a coat layer of 50 µm thick. The spectral transmittance curve of this filter is shown in Fig. 5. The near-infrared cut-off percentage of this filter was 97 %, and the visible ray transmittance thereof was 60 %. The filter was good.

Example 21:

[0091] In the same manner as in Example 20 except that triacetyl cellulose was used as the resin and a mixture of methylene chloride/methanol of 9/1 by weight was used as the solvent, a near-infrared-absorbing filter was produced. The near-infrared cut-off percentage of this filter was 97 %, and the visible ray transmittance thereof was 60 %. The filter was good.

Example 22:

[0092] In the same manner as in Example 20 except that 0.40 % by weight, relative to the fluorene copolyester obtained in Example 1, of di-immonium dye of formula (13), 0.10 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-

dithiolate and 0.05 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, a near-infrared-absorbing filter was produced. The near-infrared cut-off percentage of this filter was 97 %, and the visible ray transmittance thereof was 60 %. The filter was good.

5 Example 23:

[0093] In the same manner as in Example 20 except that 0.50 % by weight, relative to the fluorene copolyester obtained in Example 1, of di-immonium dye of formula (13), 0.15 % by weight of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate and 0.08 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) were used, 10 a near-infrared-absorbing filter was produced. The near-infrared cut-off percentage of this filter was 97 %, and the visible ray transmittance thereof was 60 %. The filter was good.

Example 24:

15 [0094] The fluorene copolyester that had been prepared in Example 1 was mixed with 0.6 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, 0.1 % by weight of phthalocyanine dye (EX Color 801K, manufactured by Nippon Shokubai) and 0.1 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai), and dispersed in methylene chloride. An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon.

20 [0095] The thus-prepared, near-infrared-absorbing film was laminated on a transparent conductive glass sheet having a near-infrared-reflecting layer thereon. The glass sheet had a multi-layered structure of zinc oxide/silver/zinc oxide/silver/zinc oxide, in which the silver thickness per one layer was 130 Å. Thus was produced a near-infrared-shielding panel having the structure of Fig. 1-B. The spectral transmittance curve of this panel is shown in Fig. 6. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 63 %. The panel was good.

Example 25:

30 [0096] The fluorene copolyester that had been prepared in Example 1 was mixed with 1.0 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate, 0.2 % by weight of phthalocyanine dye (EX Color 801K, manufactured by Nippon Shokubai), 0.3 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) and 2.3 % by weight of di-immonium dye of formula (13), and dispersed in methylene chloride. An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon.

35 [0097] The thus-prepared, near-infrared-absorbing film, and a transparent conductive film having a near-infrared-reflecting layer (IDIXO, manufactured by Idemitsu Kosan) on a shape-retaining layer of an acrylic sheet having a thickness of 3 mm. Thus was produced a near-infrared-shielding panel having the structure of Fig. 1-A. The spectral transmittance curve of this panel is shown in Fig. 7. The near-infrared cut-off percentage of this panel was 97 %, and the visible ray transmittance thereof was 60 %. The panel was good.

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Comparative Example 1:

45 [0098] The fluorene copolyester that had been prepared in Example 1 was dispersed in methylene chloride along with 5.5 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate prepared in Example 1, and 1.5 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai). An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon. The spectral transmittance curve, G, of this film is shown in Fig. 8. The film had a high near-infrared cut-off percentage of 98 %, but had a low visible ray transmittance of 25 %. Therefore, the film was not good.

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Comparative Example 2:

55 [0099] The fluorene copolyester that had been prepared in Example 1 was dispersed in methylene chloride along with 0.05 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate prepared in Example 1, 0.01 % by weight of phthalocyanine dye (EX Color 801K, manufactured by Nippon Shokubai) and 0.01 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai). An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon. The spectral transmittance curve, H, of this film is

shown in Fig. 8. The film had a high visible ray transmittance of 85 %, but had a low near-infrared cut-off percentage of 55 %. Therefore, the film was not good.

Comparative Example 3:

[0100] The fluorene copolyester that had been prepared in Example 1 was mixed with 2.0 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate prepared in Example 1, 1.5 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) and 4.0 % by weight of di-immonium dye of formula (13), and dispersed in methylene chloride. An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon. The spectral transmittance curve, I, of this film is shown in Fig. 8. The film had a high near-infrared cut-off percentage of 98 %, but had a low visible ray transmittance of 40 %. Therefore, the film was not good.

Comparative Example 4:

[0101] The fluorene copolyester that had been prepared in Example 1 was mixed with 0.05 % by weight, relative to the copolyester, of nickel bis-1,2-diphenyl-1,2-ethene-dithiolate prepared in Example 1, 0.01 % by weight of phthalocyanine dye (EX Color 803K, manufactured by Nippon Shokubai) and 0.05 % by weight of di-immonium dye of formula (13). An adhesive polyester film (A4100 of 0.125 mm thick, manufactured by Toyobo KK) was coated with the resulting dispersion, and dried at 120°C. The resulting film had a near-infrared-absorbing layer of 0.01 mm thick formed thereon. The spectral transmittance curve, J, of this film is shown in Fig. 8. The film had a high visible ray transmittance of 82 %, but had a low near-infrared cut-off percentage of 70 %. Therefore, the film was not good. The data obtained hereinabove are summarized in the following Table 1.

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Table 1

Examples	Formation of Near-Infrared-Absorbing Film	Visible Ray Transmittance (%)	Near-Infrared Cut-Off Percentage (%)
2	Casting	70	97
3	Casting	70	97
4	Melt Extrusion	65	97
5	Melt Extrusion	64	97
6	Melt Extrusion	65	97
7	Casting	60	95
8	Casting	62	95
9	Casting	60	97
10	Casting	60	97
11	Casting	63	97
12	Casting	60	97
13	Casting	63	97
14	Casting	60	95
15	Coating	60	97
16	Coating	60	97
17	Coating	60	97
18	Coating	60	97
19	Coating	60	97
20	Coating	60	97
21	Coating	60	97

	22	Coating	60	97
5	23	Coating	60	97
10	24	Coating	63	97
15	25	Coating	60	97
20	Comparative Examples			
25	1	Coating	25	98
30	2	Coating	85	55
35	3	Coating	40	98
40	4	Coating	82	70

30 INDUSTRIAL APPLICABILITY

[0102] As has been described in detail hereinabove, the present invention provides a single-layered or multi-layered, near-infrared-absorbing film or a multi-layered near-infrared-absorbing panel, which comprises an absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer material. The film and panel absorb near-infrared rays as emitted by image output devices such as plasma displays, lighting appliances or the like so as to cut off the penetration of the rays through the film, thereby preventing remote-control infrared communication ports that employ the rays falling within an infrared range for communication from malfunctioning and even preventing the appliances to be controlled by those remote-control devices from malfunctioning. In addition, they are used for detecting forged cash cards, ID cards, etc.

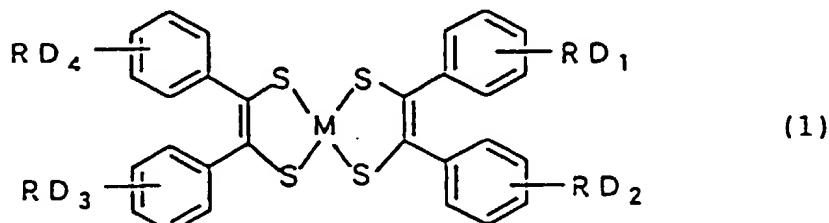
40 BRIEF DESCRIPTION OF THE DRAWINGS

[0103] Fig. 1 shows some embodiments of the structure of the near-infrared-absorbing film or panel of the invention; Fig. 2 shows the spectral transmittance curve of the panel of Example 2; Fig. 3 shows the spectral transmittance curve of the panel of Example 7; Fig. 4 shows the spectral transmittance curve of the panel of Example 15; Fig. 5 shows the spectral transmittance curve of the filter of Example 20; Fig. 6 shows the spectral transmittance curve of the panel of Example 24; Fig. 7 shows the spectral transmittance curve of the panel of Example 25; Fig. 8 shows the spectral transmittance curves of the films of Comparative Examples 1 to 4.

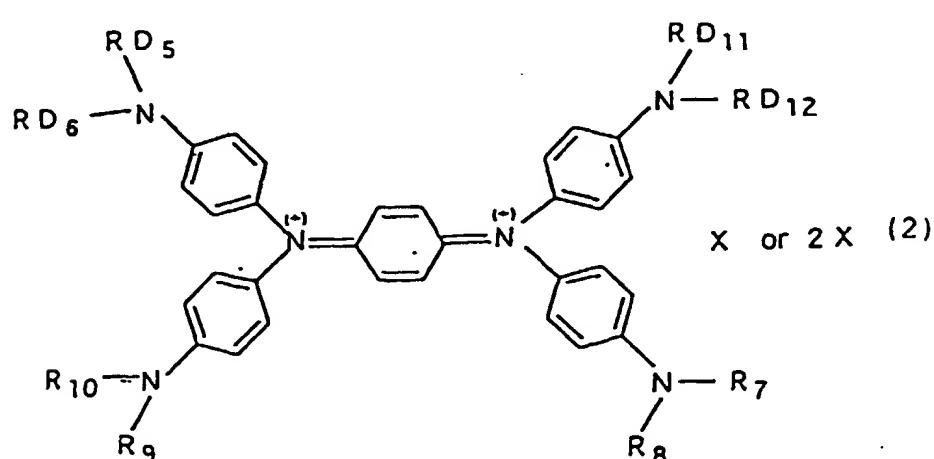
50 Claims

1. A multi-layered, near-infrared-absorbing film or panel, which comprises an absorbing layer of a near-infrared-absorbing dye as dispersed in a transparent polymer resin.
- 55 2. A near-infrared-absorbing film, which is formed from a uniform solution of a near-infrared-absorbing dye and a polymer resin in a solvent in a casting method or a coating method, or from a melt mixture of the dye and the polymer resin in a melt extrusion method, or from a uniform mixture of a near-infrared-absorbing dye and a monomer in a polymerization method of polymerizing and solidifying it.

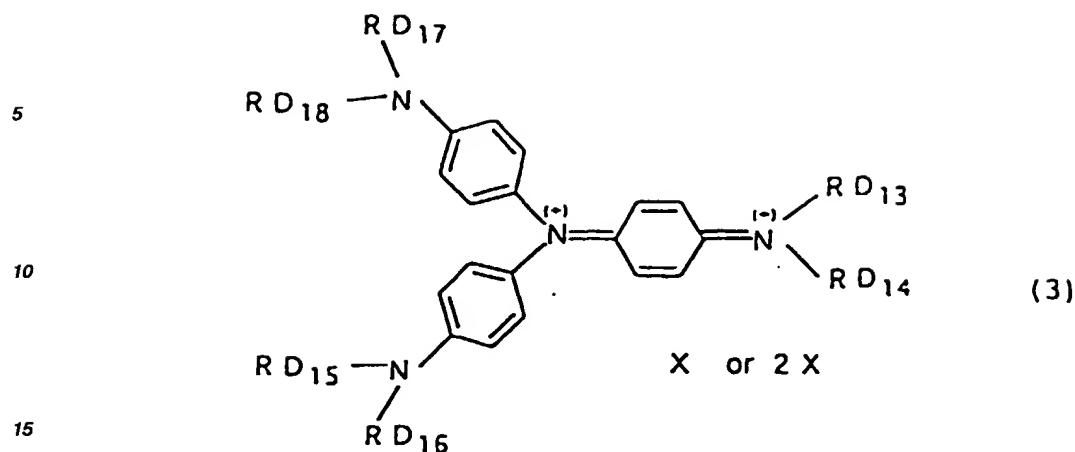
3. The multi-layered, near-infrared-absorbing film or panel as claimed in claim 1, wherein the absorbing layer is a transparent plastic film as formed through vapor deposition of a near-infrared-absorbing dye along with a metal, a metal oxide or a metal salt.
- 5 4. The multi-layered, near-infrared-absorbing film or panel as claimed in claim 1, wherein the absorbing layer is a laminate composed of plural layers of at least one or more selected from the films of claim 2 or 3.
- 10 5. The multi-layered, near-infrared-absorbing film or panel as claimed in claim 1, 3 or 4, which comprises the near-infrared-absorbing film of claim 2 and at least one of an electromagnetic radiation-absorbing layer, an antireflection layer, a shape-retaining layer and an ultraviolet-absorbing layer.
- 15 6. The multi-layered, near-infrared-absorbing film or panel as claimed in claim 1, 3, 4 or 5, of which the light transmittance profile is such that the visible ray transmittance is not lower than 55 % and the near-infrared ray transmittance is not higher than 5 %, when the near-infrared-absorbing film of claim 1 is laminated with a radiation-resistant glass sheet capable of reflecting heat radiations. ✓
- 20 7. A near-infrared-absorbing film comprising a near-infrared-absorbing dye, wherein the dye is a mixture of at least one or more selected from phthalocyanine-metal complexes, aromatic dithiol-metal complexes of the following general formula (1), and aromatic di-immonium compounds of the following general formulae (2) and (3):



30 wherein RD₁ and RD₂ each represents an alkylene group having from 1 to 4 carbon atoms, an aryl group, an aralkyl group, a fluorine atom or a hydrogen atom; and M represents a tetradentate transition metal:

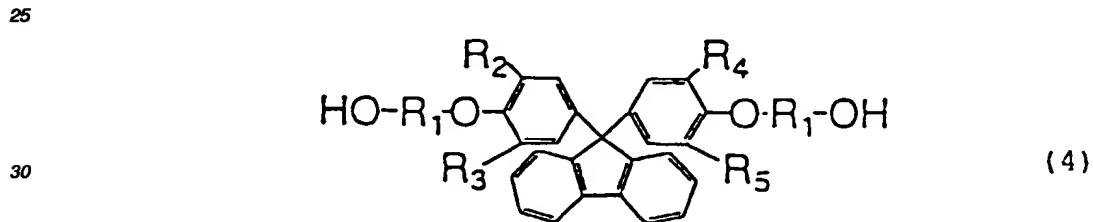


50 wherein RD₅ to RD₁₂ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a mono-valent or divalent anion, which is a counter-ion for neutralizing the ionized compound:

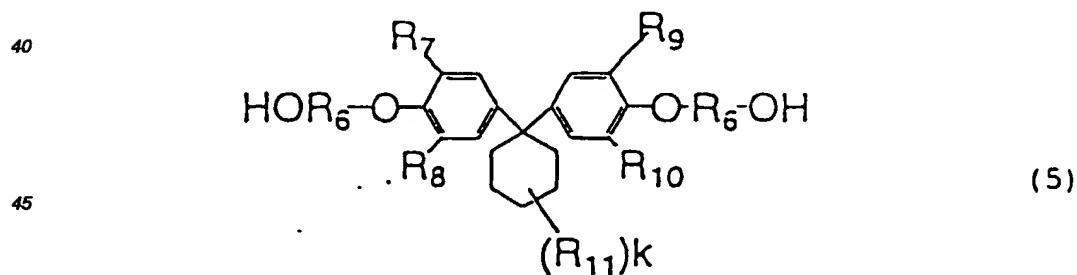


20 wherein RD₅ to RD₁₈ each represent an alkyl group having from 1 to 10 carbon atoms; and X represents a mono-
valent or divalent anion, which is a counter-ion for neutralizing the ionization.

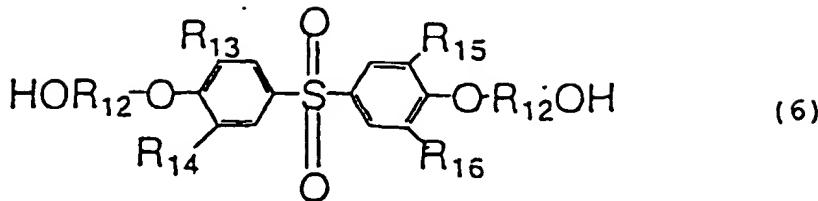
- 25 8. The near-infrared-absorbing film as claimed in claim 7, for which the near-infrared-absorbing dye is uniformly mixed
with a polymer resin in a solvent, the polymer resin being a polyester resin as copolymerized with at least 10 mol%
or more of at least one selected from aromatic diols of general formulae (4) to (9):



35 wherein R₁ represents an alkylene group having from 2 to 4 carbon atoms; R₂, R₃, R₄ and R₅ each represent a
hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or
different:



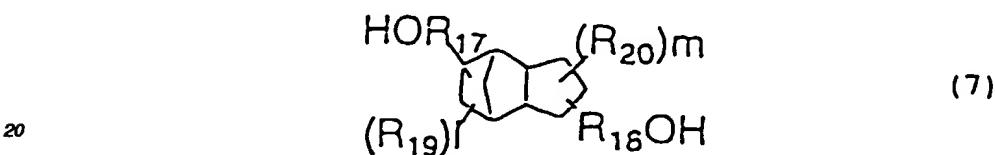
50 wherein R₆ represents an alkylene group having from 1 to 4 carbon atoms; R₇, R₈, R₉, R₁₀ and R₁₁ each represent a
hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or
different; and k represents a natural number of from 1 to 4:



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wherein R₁₂ represents an alkylene group having from 1 to 4 carbon atoms; R₁₃, R₁₄, R₁₅ and R₁₆ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different:

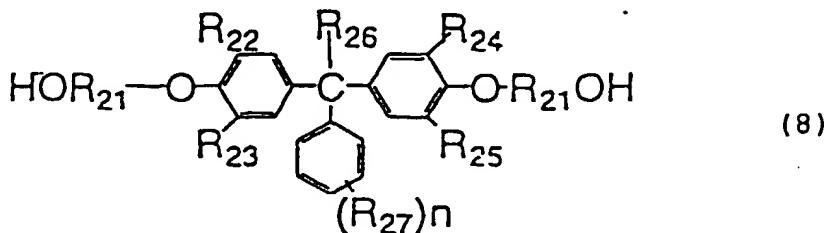
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wherein R₁₇ and R₁₈ each represent an alkylene group having from 1 to 4 carbon atoms, and these may be the same or different; R₁₉ and R₂₀ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different; and I and m each represent a natural number of from 1 to 8:

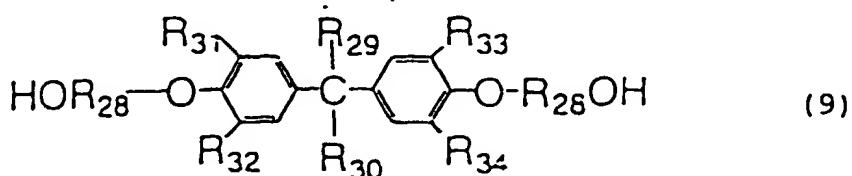
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wherein R₂₁ represents an alkylene group having from 1 to 4 carbon atoms; R₂₂, R₂₃, R₂₄, R₂₅, R₂₆ and R₂₇ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different; and n represents a natural number of from 0 to 5:

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wherein R₂₈ represents an alkylene group having from 1 to 4 carbon atoms; R₂₉ and R₃₀ each represent an alkyl group having from 1 to 10 carbon atoms, and these may be the same or different; R₃₁, R₃₂, R₃₃ and R₃₄ each represent a hydrogen atom, or an alkyl, aryl or aralkyl group having from 1 to 7 carbon atoms, and these may be the same or different.

9. The near-infrared-absorbing film as claimed in claim 7 or 8, which is formed in the polymerization method of claim 2.

- 10. The multi-layered, near-infrared-absorbing film or panel as claimed in claim 1, 3 or 6, which comprises the film of claims 7, 8 or 9.**

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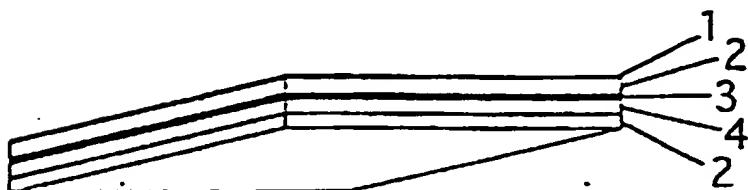
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Fig. 1

A



B



C

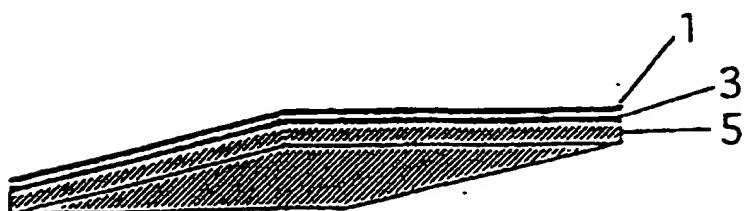


Fig. 2

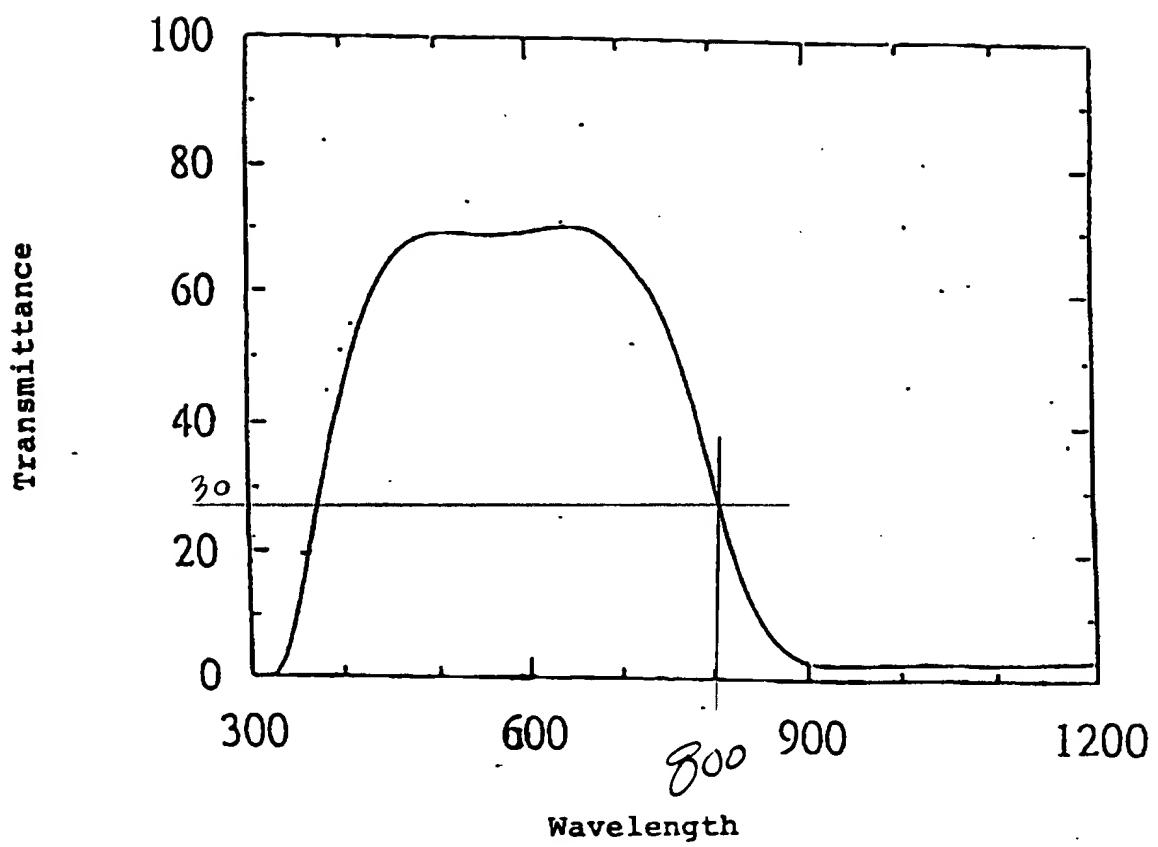


Fig. 3

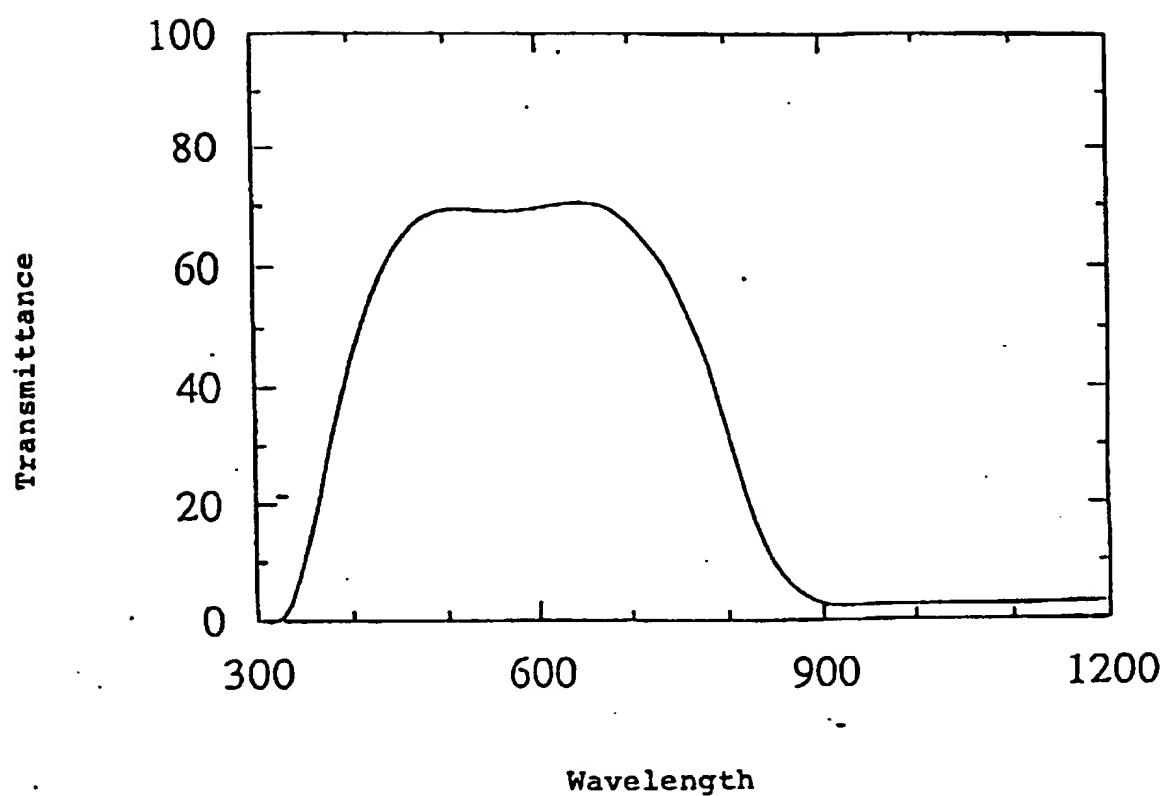


Fig. 4

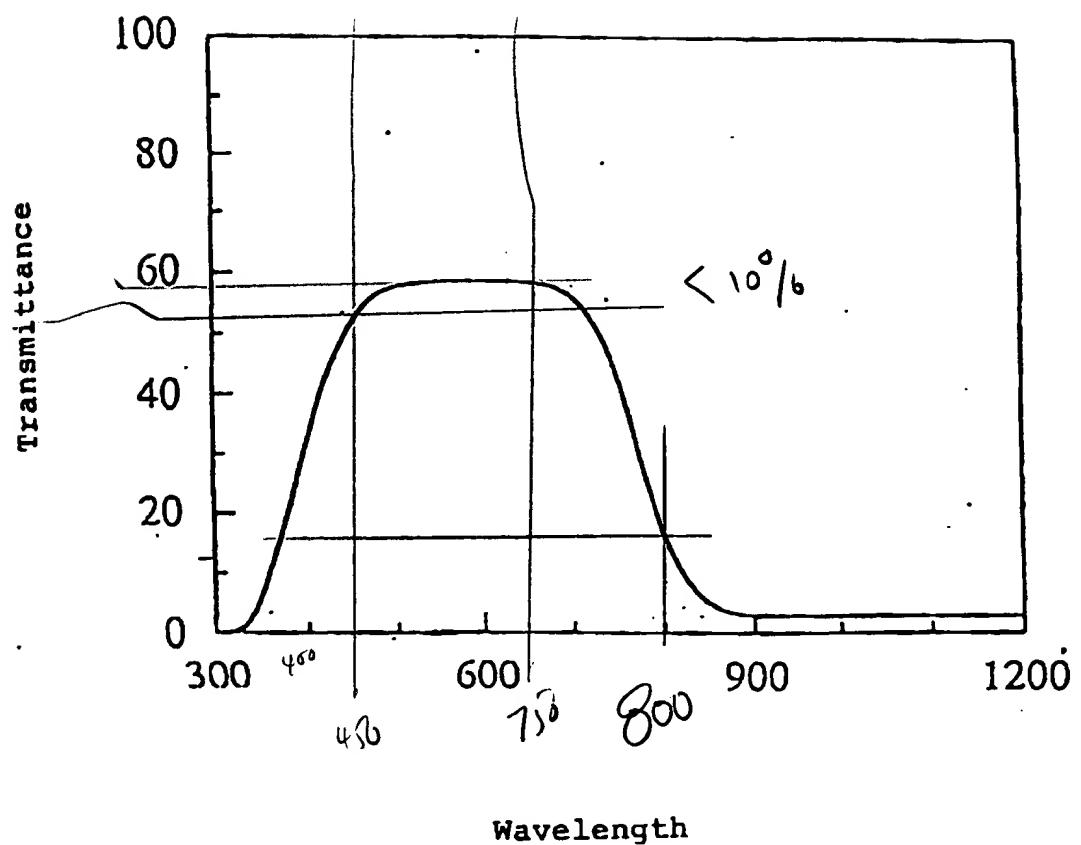


Fig. 5

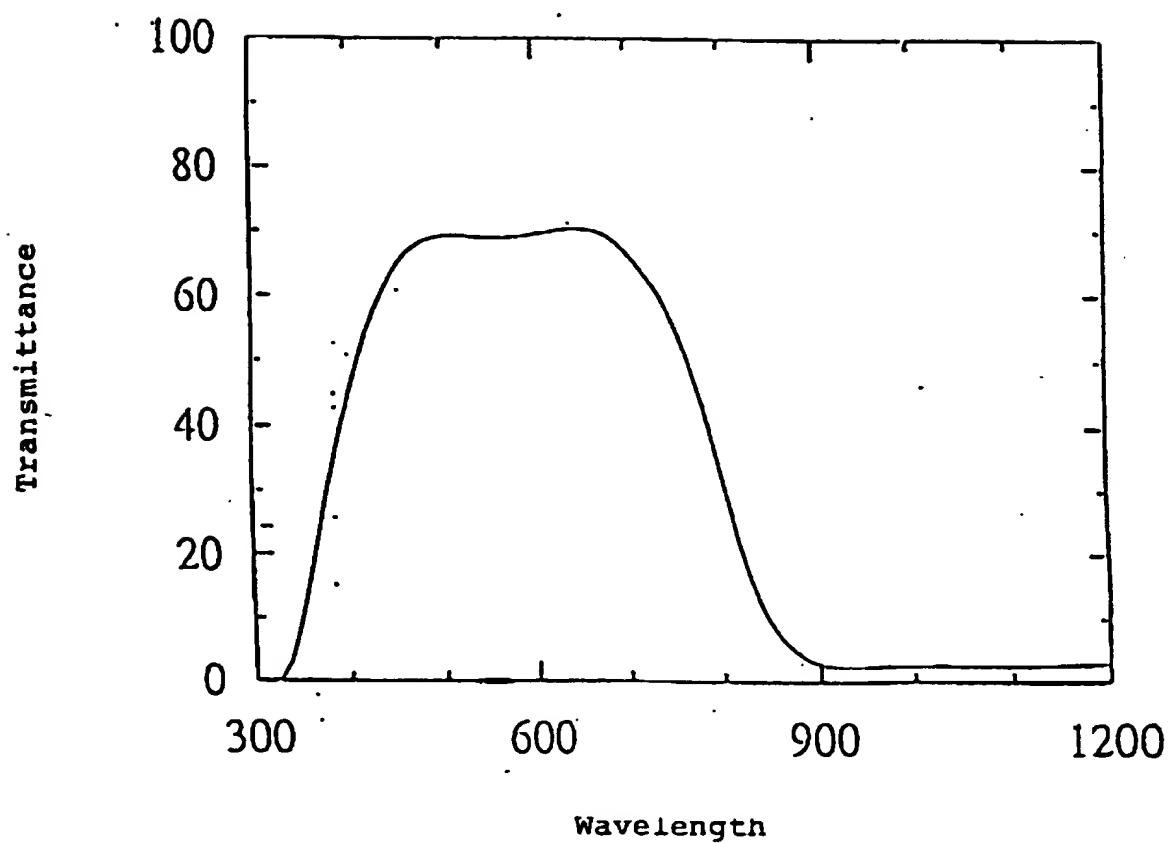


Fig. 6

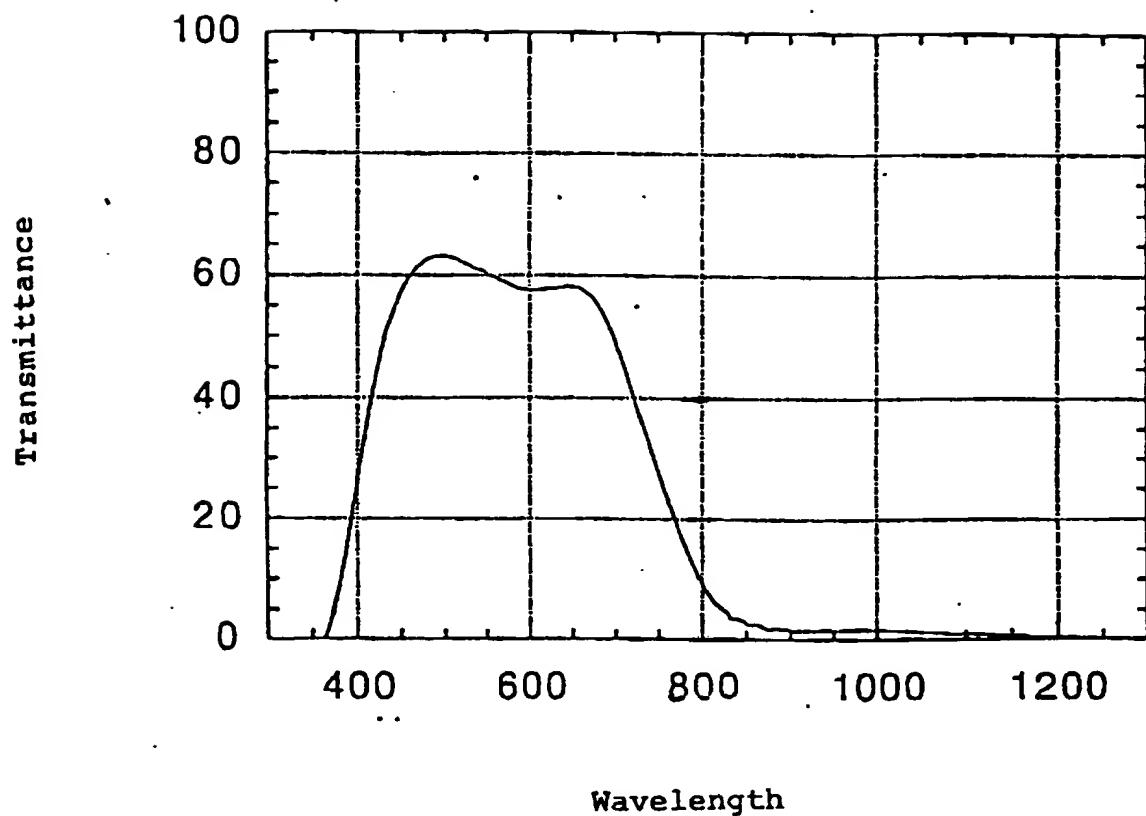


Fig. 7

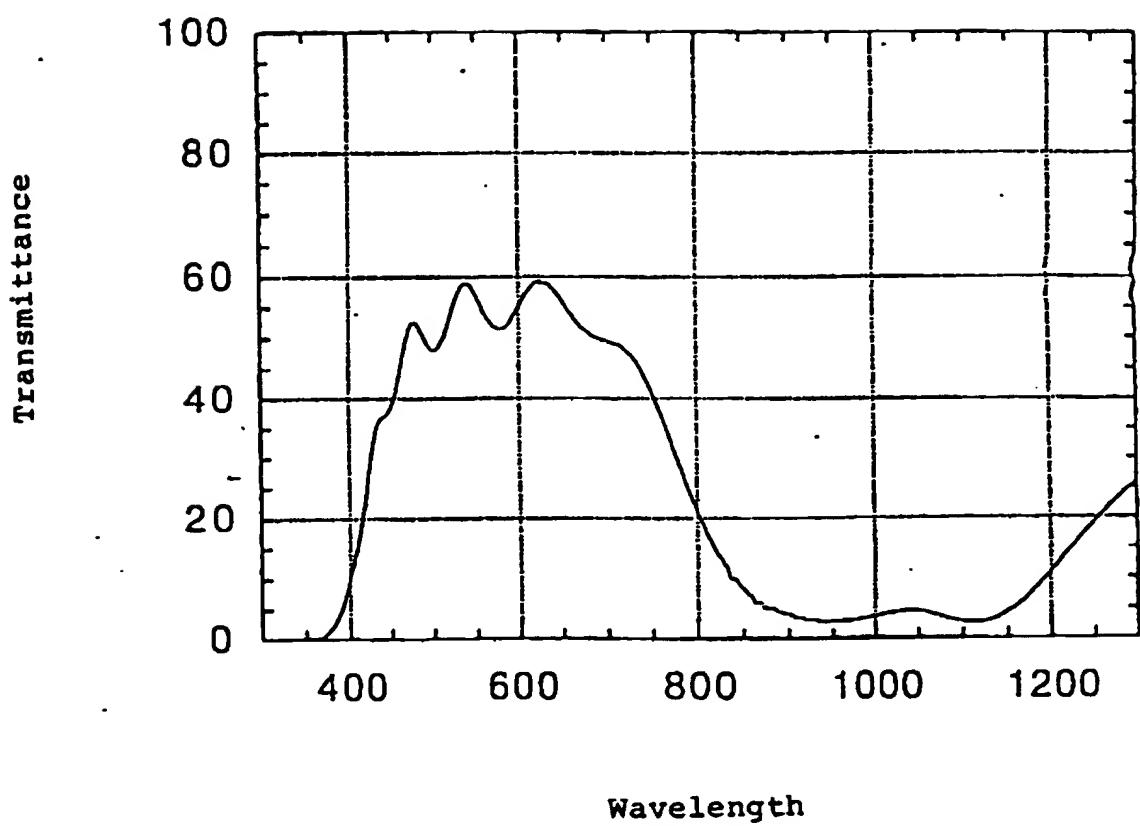
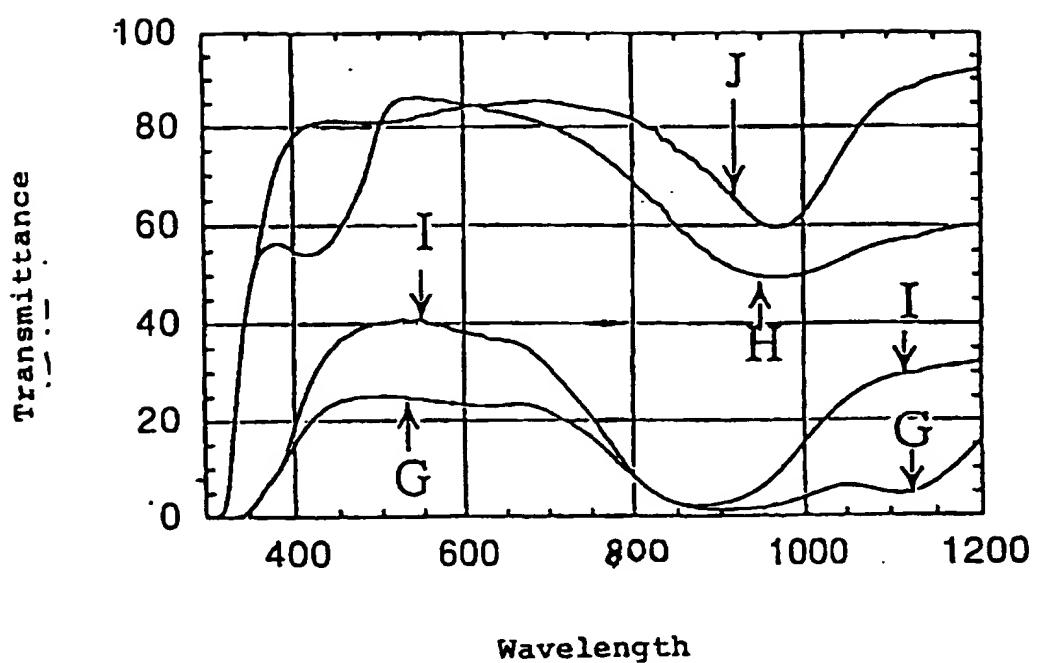


Fig. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/01341

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ B32B27/18, C08G63/66, C08G63/688, C08L67/02, C08L101/00,
G02B5/22, F21V9/04, C08K5/45, C08K5/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ B32B27/18, C08G63/66, C08G63/688, C08L67/02, C08L101/00,
G02B5/22, F21V9/04, C08K5/45, C08K5/29

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996
Jitsuyo Shinan Keisai Koho	1994 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 6-194517, A (Mitsui Toatsu Chemicals, Inc.), July 15, 1994 (15. 07. 94), Column 1, lines 9 to 12, 31 to 37; column 2, lines 1 to 10; column 5, lines 38 to 49 (Family: none)	1, 2, 6, 7, 9, 10
A	JP, 6-200113, A (Nippon Zeon Co., Ltd.), July 19, 1994 (19. 07. 94), Column 1, lines 13 to 20 (Family: none)	1 - 10

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

July 16, 1997 (16. 07. 97)

Date of mailing of the international search report

July 29, 1997 (29. 07. 97)

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